"THE SEPARATION OF PARAFFIN WAXES IN THEORY AND PRACTICE".

A T H E S I S

Presented by

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C O N T E N T S.

SECTION III (Continued).

I N T R O D U C T I O N.

In recent years, one section of the Research carried out in the Department of Oil Engineering and Refining, University of Birmingham, has been concerned with the application of Phase Rule principles to equilibria existing in systems of particular importance to the Petroleum Industry. It seemed desirable to extend this theme in a study of the fractional melting process for the separation of paraffin waxes of different melting points, with the ultimate object of applying, if possible, any equilibrium diagram thus obtained, to the sweating process employed industrially in the production of paraffin wax.

Many misleading and contradictory data relating to paraffin wax and the sweating process are to be found in the technical literature. No justification is therefore needed for the inclusion of the fairly comprehensive - but non-critical - review of the subject which constitutes the first of the three sections of this Thesis. This is essential for the full appreciation of the various special considerations necessary in the study of this problem.

Sections 2 and 3 are concerned respectively with the separation of paraffin waxes in theory and in practice, and the various stages of the work are presented in the order in which they were completed. The attempt to apply Phase Rule principles in a study of a substance so complex in nature resulted in the almost inevitable lines of approach which proved to be of

negative value. These are included in the account, in general, only if they proved to be essential in leading to the final solution of the problem. The initial difficulties, encountered especially in the elucidation of the equilibrium diagram, were gradually eliminated, and it is believed that the solution of the problem presented in these pages has been established on a logical and sound basis.

The work described herein will, it is hoped, provide the data for two or more original papers to be submitted for publication in the near future.

SECTION I

SECTION I - THE SEPARATION OF PARAFFIN WAXES

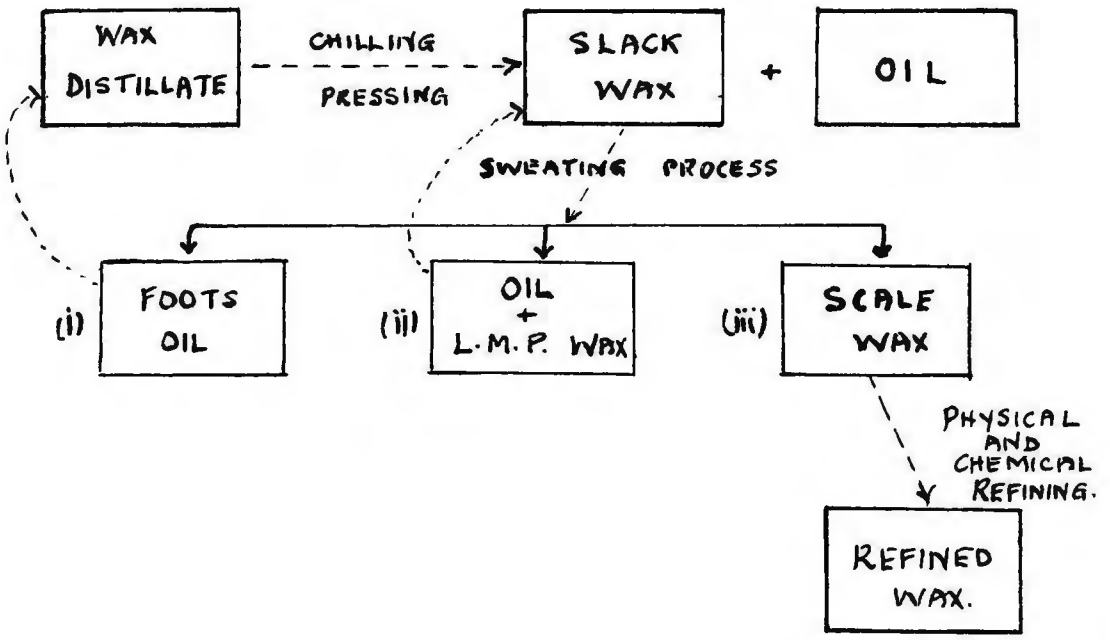
LITERATURE SURVEY.

Introduction

The production of paraffin wax from wax-bearing distillate may be considered to take place in the following stages :-

(1) Partial removal of the oil by chilling and filter pressing,
(2) Removal of oil and waxes of low melting point by the process of fractional melting - the so-called "sweating" process, and
(3) Chemical refining of the sweated wax.

The stages are conveniently illustrated by the following diagram:-



The research project is concerned primarily with the sweating stage in the production, and in the following pages a survey is made of the published work relating to the various factors which may affect the efficiency of the operation. This review of the literature is given in five sections, in which are considered respectively :-

(a) The Sweating Process.
(b) Crystallisation of Wax.
(c) Composition of Wax.
(d) Solubility of Wax in Oil.
(e) Recent Patent Literature.

(a) The Sweating Process

It is not proposed to give a detailed account - such as may be found in appropriate text-books - of the treatment accorded the wax distillate, but a few essential details only are appended for the purposes of illustration and future reference.

The wax distillate is chilled to a temperature depending on the desired pour point of the oil, after which it is pumped through a filter press. The crude wax - usually termed "slack-wax" - thus produced, is a solid normally of melting point 100-105°F. and oil content of less than 50%, but these properties vary considerably according to refinery practice. The slack wax is liquefied, transferred to the sweating plant, allowed to cool to solid consistency and then subjected to a heat treatment commonly termed "sweating". This operation consists essentially in removing first the oil and then the lower melting point waxes by gradually increasing the temperature of the mass over a period of some hours, and continuing until wax of the required melting point remains. The principle of operation is based on the fact that the various waxes comprising the slack wax have progressively higher melting points. The fractions removed contain valuable products, and re-sweating is therefore an important feature of the commercial process. Innumerable combinations of re-sweating are possible to give a wide range of products differing in melting point and oil content.

In this process of fractional melting, accurate control and regulation of temperature throughout the system, and adequate means of draining the liquid formed during the operation are essential, but satisfactory sweating is dependent also on other factors, the chief being the size and shape of the slack-wax crystals, which in turn, vary according to the treatment of the slack wax.

From the evidence advanced by many workers it seems that wax may crystallise in the form of plates, needles, or leaflets; an amorphous form is also possible. The plate crystal represents the most stable form, but it is generally recognised that large needle shaped crystals are essential for satisfactory sweating. It would appear that the needle structure is such that the interstices which form between the crystals on melting

remain open, thus allowing the liquid consisting of the oil and low melting point (L.M.P.) waxes to drain from the solid or higher melting point (H.M.P.) wax. Other crystal forms apparently do not provide this convenient means of drainage, but rather hinder the process by occluding oil and melted wax. Crystallisation of wax from wax distillate appears to be influenced by many factors, the more important being the distillation and boiling range of the distillate cut, cooling rate, viscosity of medium, and especially by the presence of impurities which may be colloidal in nature and which are adsorbed by the wax and thus modify or inhibit crystallisation. It is not generally accepted, however, that all these factors affect the crystallisation. In view of the importance of wax crystal structure in relation to sweating, a summary is given of the information concerning the forms in which wax may be obtained.

(b) Crystallisation of Wax

It was originally believed that wax was present in crude petroleum only in an amorphous form, but that it was converted into a crystalline structure by distillation or heat treatment. This view was supported by the conclusions of Zaloziecki[2], who extracted a waxy residue from Klenczany crude with amyl alcohol to obtain a crystalline residue and amorphous extract. However, as a result of a microscopic study of the crystalline form of waxes, Gurwitsch[3] suggested that the so-called amorphous form was not truly amorphous but consisted of minute crystals, the development of which had been retarded by the presence of resinous and asphaltic bodies, and especially by certain high viscosity oily components.

From a photomicrographic study, Padgett, Hefley and Henriksen[4] concluded that the actual nature of the wax was the essential factor in crystallisation, although the presence of asphaltic material and oil had some effect, especially on the size of crystals. According to Fussteig,[5] the inhibition of wax crystallisation from certain heavy wax distillates may be attributed to surface tension effects caused by the presence of two protective films surrounding the wax particle. The outer film, removable by treatment with sulphuric acid, consists of asphaltic and resinous hydrocarbons, but the inner film consists of high molecular weight oily compounds which may be removed only by special treatment with a solution of phenol (5%) in benzene (95%).

Rhodes, Mason and Sutton[6] found that the crystalline form of six fractions obtained by a Laboratory sweating of Pennsylvanian slack wax was dependent on the rate of cooling. At all rates of cooling, plates were first formed, slow cooling resulting in the formation of plates only. On rapid cooling (0·1°C. per minute) it was found, however, that the initially formed plates curled at the edges and rolled into needles, a mixture of needles and plates being obtained on solidification.

Buchler and Graves[7] observed that pure paraffin wax crystallises in plates whether crystallised from solution or frozen from the molten state. On recrystallisation from ethylene dichloride at 40°F. two impurities were removed, oil and an unknown substance which the authors term "soft-wax". It was concluded that crystal form is governed by (1) the viscosity of the oil and molecular weight of the stock and (2) the content of soft-wax impurity, which when present in small amounts causes impure waxes to crystallise in the form of needles, but when in large amounts, promotes amorphous or microcrystalline structure. Of interest in this connection is a later paper by Graves[8] in which he states that synthetic normal paraffin hydrocarbons containing 22, 23, 30 & 40 carbon atoms, having melting points of 44·3°C; 47·8°C; 65 - 66°C; and 80·5 - 81°C; respectively, form plate crystals apparently identical with those of the paraffin waxes. Gascard[9] also prepared certain synthetic hydrocarbons of high molecular weight which, he found, crystallised as plates when pure, but as needles when impurities were present. Carothers[10] and his co-workers observed that the n-paraffins having respectively 62, 64 and 70 carbon atoms, crystallised from hot butyl acetate or benzene in the form of minute needles.

According to Jones and Blachley,[11] the differences between soft amorphous waxes and hard crystalline waxes are associated with variation in surface tension caused by the adsorption on the wax crystals of an impurity - of the "soft-wax" type (Buchler and Graves) - the effect depending on the degree of dispersion and the amount adsorbed. Sachanen, Zherdeva and Vasilyev,[12] and also Bestushew,[13] are in substantial agreement with this view, but consider that the change in the basic structure is caused by the presence of ceresines which may be present in crude petroleum and which are separated from the paraffin by distillation.

Three crystal forms - plate, needle and malcrystalline (having no definite form) - were distinguished by Ferris, Cowles, and Henderson,[14] who also found that under suitable conditions the needle and especially the malcrystalline form were able to impress their form on plate crystals. It was concluded

that the crystal form is an inherent property of the wax and is independent of other factors, such as the viscosity of the solvent. Thus, a pure plate will invariably crystallise as a plate, and a pure needle as a needle, a view substantiated by the observations of Buchler and Graves[7] but contrary to those of Gurwitsch[3] and others. Carpenter,[15] however, has found that low viscosity of the medium favours the formation of plates whilst high viscosity assists in the formation of needles, thus agreeing with the observations of Tanaka,[16] who also concluded that the crystal form was not affected by the chemical nature of the wax.

Katz[17] concluded that crystal form is affected by concentration, although needles are invariably formed from plates in an irreversible transformation. Fussteig[18] has observed that needles may be formed from plate crystals when a warmed wax distillate containing plates is suddenly cooled with cold water. Within limits, the greater the temperature difference between the water and the distillate, the longer and thicker are the needle crystals.

From X-ray studies, Clark[19] has determined that the crystal spacing is a function of many variables including melting point, rate of crystallisation, and source of the wax.

Of interest in connection with wax crystallisation is a recent paper by Leslie and Heuer[20] who have examined the crystallisation of a number of synthetic n- and iso- paraffins, cycloparaffins, and aromatic compounds, boiling within the gasoline range. Crystallisation behaviour appears to be influenced by the nature of the molecule, as long chain molecules tended to form long prisms whereas condensed molecules crystallised in polyhedrons of nearly equal dimensions. It was also observed that the compounds differed considerably in the ease with which the crystals formed, the n-paraffin and aromatic compounds growing more rapidly than the cyclo- or iso-paraffins.

(c) Composition of Wax.

Attempts have been made in many researches to elucidate the composition of paraffin wax, and there now seems little doubt that n-paraffins usually predominate. Hydrocarbons of at least one other type may also be present to some extent, but there is no general agreement as to whether these belong to the iso-paraffin or naphthenic series. The evidence, however, tends to favour the presence of iso-paraffins.

By repeated fractionation of wax from Scotch shale oil, Francis[21] and his co-workers were able to isolate a number of constant boiling fractions which were later studied by Piper, Brown and Dyment[22] who showed, from X-ray analysis, that the crystal spacings coincided with those obtained by Muller and Saville[23] for synthetic n-paraffins. Fischer and Schneider[24] had previously failed to detect the presence of iso-paraffins in wax from lignite tar, although solid iso-paraffins were present in the oil obtained by low temperature retorting. The solids obtained in the Fischer-Tropsch process have recently been examined and found to consist of n-paraffins, although there is some evidence for the presence of iso-paraffins of molecular formula $C_{80}H_{40}$ and $C_{150}H_{302}$.[25] Carpenter[26] identified n-paraffins in wax from Burma crude and also found some evidence for the presence of iso-paraffins. More recently, Konaka[27] has examined a wax fraction boiling over a range of 10°C. (370°-380°) obtained from Fuschan shale oil. By fractional precipitation from an alcohol/benzene solution, 13 n-hydrocarbons of melting point 28·2 - 80·6°C., having melting point and other physical properties similar to the synthetic n-paraffins of Krafft,[28] and 8 iso-hydrocarbons of melting point 22·6 - 78·6°C. were isolated in the ratio:- normal : iso= 4:1 (approximately).

Ferris, Cowles and Henderson[29] prepared waxes by crystallisation from ethylene dichloride at -18°C. followed by distillation under vacuum of less than 1 m.m. mercury, and obtained fractions having melting points considerably lower than the melting points of n-paraffins normally present in the wax range. From the study of a very complete set of physical data it was concluded that other hydrocarbons - probably iso-paraffins - were present in the wax fractions, a view supported by the X-ray diffraction experiments of Clark and Smith[30], who found that the waxes prepared by these workers contained the lower melting iso-paraffins to the extent of at least 20%. More recently, however, Mair and Schicktanz[31] have performed combustion analyses on these waxes, employing a method which has been proved to give results of great accuracy, and have shown that whilst the higher melting point fractions are composed of n-paraffins, those of lower melting point are composed chiefly of cyclic hydrocarbons.

Evidence for the presence of cyclic hydrocarbons in undistilled wax is provided by Muller and Pilat.[32] Fractions of wax of different melting points were extracted from asphalt, and from a study of the melting points in conjunction with combustion analyses, iodine numbers, and temperature/viscosity relations, the authors conclude that the presence of members of the naphthenic series is established.

Employing the polarising microscope and X-ray diffraction methods, Yannaquis[33] found two crystal forms present in Pechelbronn wax - (a) a triclinic form existing as separate crystals or as a network which, he concluded, were composed of saturated cyclic hydrocarbons with long chains, and (b) a monoclinic form, existing as needles of fibrous structure, consisting of open chain paraffins with short branches.

McKitterick, Henriques, and Wolff[34] in a recent study of the physical properties of wax, have concluded that high melting point distillate fractions contain large proportions of n-paraffins, whereas in the lower melting point fractions, iso-paraffins, naphthenes and aromatics (in this order) may predominate. The higher melting fractions of residues differ, as n-paraffins do not predominate. There is also evidence that the composition of distillate waxes is independent of the nature of the crude, whereas the properties of waxes from residues are affected by the nature of the parent crude.

The deductions from all the above researches are based on studies of the physical properties of waxes, but evidence of a chemical nature is supplied by Nametkin and Nifontora.[35] By treating wax with dilute nitric acid, these workers obtained tertiary nitrogen compounds and concluded that isoparaffins were present in the wax to the extent of 25 - 30%.

Kolvoort, Moser, and Verver[36] have recently studied the waxes produced by distillation of Java and Roumanian crudes, and have concluded that a stage is reached in the distillation where higher boiling fractions contain wax of poor crystalline character, and which shows a high oil retention. This latter property, which is particularly evident with the higher wax fractions from Roumanian crude, is attributed to the presence of iso-paraffins. The presence of solid cyclic hydrocarbons could not be detected, and in this connection, the authors suggest that the positive indications of the presence of cyclic compounds obtained by some workers may be due to retained oil.

(d) Solubility of Paraffin Wax in Oil.

It was observed by Wyant[37] that the greatest loss during the sweating process occurred at the temperature at which most of the oil was removed, the loss increasing rapidly above a certain critical temperature. The significance of the latter observation is explained by the work of Myers and

Stegeman[38] on the solubility of waxes of different melting points in a wax-free oil of Sp.Gr. 0·860 @ 15°C. and boiling range (under 0·1 m.m. press) 150-170°C. A marked increase was found in the solubility of both high and low melting point waxes and their mixtures at a temperature approximately 10°C. below their respective melting points. L.M.P. waxes were found to be more soluble than H.M.P., andmixtures showed solubilities intermediate between those of the components. The presence of a solid solution of oil in wax of oil content 2 - 2·5% at room temperature, is considered by these workers to explain the necessity for performing the sweating operation at a comparatively high temperature, as the oil is retained to a temperature slightly below the melting point.

The solubility of wax in all petroleum fractions (and some other solvents) was determined by Sachanen[39] and shown to increase considerably with increase in temperature, until at the melting point the wax was miscible in all proportions with the oil. The solubility was also found to decrease with increase in melting point and specific gravity of the wax.

Sullivan, McGill, and French[40], in an investigation to determine the effect of the melting point of the wax and the viscosity of the solvent on the solubility of closely-cut wax fractions in the oil from which they were separated, showed that solubility increases with decrease in the melting point of the wax and with decrease in the viscosity of the oil. Differences in solubility due to difference in the melting point of the wax or to variations in the viscosity of the solvent, decrease with decrease in temperature.

Pyhala[41] observed that small needle crystals showed a greater tendency than large needles to dissolve in the oil present when the temperature was increased, thus giving an additional reason for the more satisfactory sweating achieved with large needles. It was also found that the loss of wax due to solution in the oil during sweating increased with higher oil content. Fussteig[5] concludes that the solubility of wax in oil is greatly influenced by the nature of the oil, the wax being more soluble in asphaltic oils.

The needle crystals prepared by Ferris[14] & co-workers were found to be very much more soluble in all solvents investigated than plate crystals of the same molecular weight. Waxes of the same melting point, however, exhibited similar solubilities in a given solvent.

(e) Patent Literature.

In view of the progress that has been made in recent years in the production of other petroleum products, it is rather surprising that no radical changes have been introduced into the manufacture of paraffin wax from wax distillate. A survey of the patent literature of the last few years shows that the patents having some connection with the sweating process may in general be included in one of the following groups :-

(a) Improvements in the recognised sweating plant.

(b) Special processes for pretreatment of the slack wax to improve its sweating properties.

(c) Production of wax by solvent methods.

Numerous improvements have been introduced in the actual sweating plant, but these incorporate, in general, means to obtain greater efficiency in heat transfer and to shorten the sweating period. These patents will not receive further treatment here. It is of interest to observe, however, that methods employing the principle of continuous sweating have been devised in recent years.[42] The main objects of such methods are to overcome the inefficiencies in the utilisation of heat and to shorten the time required for sweating. The plant is usually provided with a chamber divided into many compartments which are maintained at the desired temperatures. The wax is conducted through the plant on an endless foraminous belt and the liquid products formed during sweating are collected in receptacles located in each compartment.

The various factors which affect the sweatability of a wax have already been considered, and it is not surprising to find that a number of patents have been granted which claim to improve the sweating qualities by special pretreatment of the wax. It is claimed[43] that the finely divided or colloidal solids which promote bad crystallisation are removed from the wax by treatment of the mass, in the presence of air, with aqueous solutions of soaps of fatty or naphthenic acids, resin soaps, and especially with alkali and ammonium salts of sulphonic acids.

Sweating of slack wax in the presence of approximately 2% Pourex, Paraflow or other crystallisation regulator, is claimed[44] to result in a considerably increased yield of wax in a shorter sweating period. The regulator is removed from the wax with the foots oil and may be recovered from the latter by fractional distillation.

A high melting point wax of 95% wax content may be obtained from one of oil content of 20% by treatment of the latter at normal temperature with a wetting agent such as an aqueous solution of aromatic or polynuclear sulphonic acids, those alkylated in the necleus proving particularly effective.[45]

The addition of a wax of high needle wax content, which acts as a crystal form impressing agent, is claimed[46] to improve the sweating properties of slack wax. Needle wax is related to, but not synonymous with, needle crystals. The crystal form is affected only if the solubility relationships are such that the needles may separate from solution simultaneously with the plates.

Wax is normally surrounded with air or water during sweating, but it is claimed[47] that if an aqueous solution (10%) of alkali phosphate is employed as the medium, superior results are obtained, the rate of sweating being increased and solid wax of relatively high melting point resulting. It would appear that the alkali phosphates lower the surface tension between the oil and the wax so that the oil is more easily detached from the wax during the sweating.

Patents have been granted which claim to increase the efficiency of the sweating process by removal of some oil and low melting point wax prior to the actual sweating. A residue of considerably higher wax content which may be readily sweated, is obtained by steam distillation of low melting point wax under conditions which avoid substantial cracking, the oil and wax of low melting point being obtained as distillate.[48] Another means of removing oil from slack-wax consists in heating the wax above the average melting point, gradually cooling and simultaneously treating it with a kneading action such that the wax is allowed to alternately contract and expand during cooling. The wax-oil mixture is then discharged to a screen from which the oil drains.[49] A considerably increased yield of high melting point wax may be obtained from wax of less than 5% oil content by subjecting it to vacuum or preferably steam distillation, the distillation being continued until residue of the desired melting point remains. This may then be removed as a distillate.[50]

Methods of obtaining wax by the use of selective solvents, thus eliminating the sweating process, appear in a number of patents. Liquid propane[51, 52] or other liquefied normally gaseous hydrocarbon may be employed, but the use of propane as solvent sometimes results in the formation of wax, which owing to the particular crystal growth, is difficult to separate from the oil. It is claimed[53] that the addition of 0·05 to 0·5% triethanolamine oleate causes the wax to crystallise in an

easily removable form. Other solvents such as acetone, benzine, benzene and 96% alcohol mixtures, which substantially dissolve the oil but not the wax, are claimed[54] to be effective in the preparation of highly concentrated wax, separation from the liquid being effected by means of a continuous filter acting by suction.[55] Treatment of slack wax with n-butyl alcohol is claimed to give a high melting point wax virtually free from adhering oil. The slack-wax is broken into a form which is readily pumped, and then treated with sufficient solvent to dissolve the oil but not the wax, after which the wax is separated by centrifuging. Other solvents including acetone, ethylene dichloride, alcohol/benzene mixtures, and alcohols containing from 2 to 6 carbon atoms in the molecule may also be used, although for practical reasons n-butyl alcohol is most satisfactory.

Solvent processes are generally unsuitable for the production in sufficient yield of paraffin wax having a melting point above 60°C., but it is claimed[56] that such wax may be obtained by treating wax distillate with 10% of a solvent rich in aromatic constituents (e.g. distilled SO_2 extract from SO_2 treatment of kerosene), followed by a sweating treatment under high pressure.

Finally, it should be mentioned that fractional crystallisation has been patented[57,58] in a process in which the oil/wax mixture is liquefied and then cooled to the required temperature by counter current contact with a 2% sodium silicate solution, followed by separation of the wax from the liquid by any convenient means. By treating the wax thus produced at successively higher temperatures, a series of waxes of increasing melting points may be obtained. The success of the operation depends on (1) strict control of the cooling rate, (2) rate of agitation (3) detergent characteristics of the cooling liquid, and from a practical stand-point, (4) difference between the specific gravity of the cooling liquid and oil/wax mixture. The process of fractional crystallisation is also employed[59] in conjunction with the use of a liquefied normally gaseous solvent, the solution being chilled to the desired temperature with the resultant precipitation of the corresponding wax. More intense chilling results in the precipitation of further quantities of wax.

SECTION II

SECTION II - THE SEPARATION OF PARAFFIN WAXES IN THEORY.

Fundamental Basis of the Investigation - The Nature of Wax.

In any study involving the Phase Rule and Phase reactions, it is obvious that the initial consideration must be that of the nature of the substance. It was stated in the previous section that there is general support for the view that paraffin wax consists of a mixture of n-paraffins and may also contain hydrocarbons of at least one other type. The waxes to be employed in this study have constituents melting at least over the range 105 - 142°F. and assuming that the components are n-paraffins, it is possible for at least the following members of the series to be present.

TABLE I

n-Paraffin		M.W.	M.Pt. (°C.)	M.Pt. (°F.)	B.P.under 15 m.m.	
n-Heneicosane	$C_{21}H_{44}$	296.3	40.4	104.7	215	
n-Docosane	$C_{22}H_{46}$	310.4	44.5	112.1	224.5	
n-Tricosane	$C_{23}H_{48}$	324.4	47.4	115.3	234	
n-Tetracosane	$C_{24}H_{50}$	338.4	51.1	124.0	243	
n-Pentacosane	$C_{25}H_{52}$	352.4	53.3	127.9	259	
n-Hexacosane	$C_{26}H_{54}$	366.4	56.6	133.9	262	
n-Heptacosane	$C_{27}H_{56}$	380.4	59.5	139.1	270	
n-Octacosane	$C_{28}H_{58}$	394.4	61.6	142.9	278	

Information concerning the state or nature of paraffin wax may be obtained from a consideration of the melting of wax.

Now a pure substance is characterised by a sharp melting point, this being the temperature at which, on heating, the entire mass melts, or/on cooling, the entire mass of liquid solidifies. Paraffin wax, however, does not possess a sharp melting point and the melting or solidification processes take place over a temperature range. It was first suggested by Gurwitsch[60.] that the single n-paraffins are partially isomorphous with regard to each other, and that during the solidification of the paraffin wax, solid solutions and not chemically pure compounds separate. In the case of non-polar organic compounds, three conditions must normally be satisfied before two substances can form solid solutions :-

(1) their chemical constitutions must be analogous:

(2) the crystal structures must be similar:

(3) their molecular volumes must be nearly equal:

Applying these conditions to the n-paraffins included in Table I, it is reasonable to suggest that there is a greater possibility of solid solution formation between e.g. n-octacosane and n-heptacosane than between n-octacosane and n-heneicosane. Assuming, then, that the paraffin wax consists of members of the n-paraffin series, it would be expected that on solidification, the components would not all simultaneously solidify to

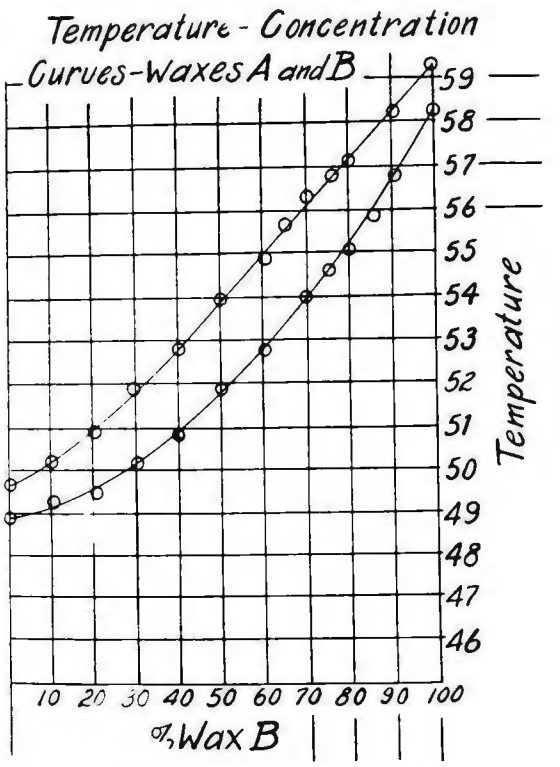

Temperature - Concentration
Curves - Waxes A and B
59
58
57
56
55
54
53
52
51
50
49
48
47
46
Temperature
10 20 30 40 50 60 70 80 90 100
% Wax B

FIG. 1.

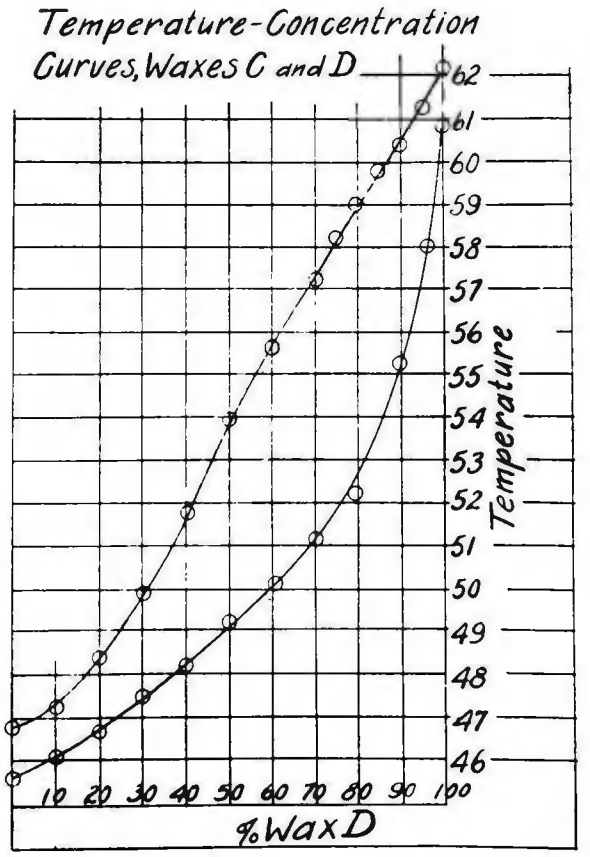

Temperature-Concentration
Curves, Waxes C and D
62
61
60
59
58
57
56
55
54
53
52
51
50
49
48
47
46
Temperature
10 20 30 40 50 60 70 80 90 100
% Wax D

FIG 2.

form one solid solution, but that different solid solutions would successively separate - the first to be formed consisting of two or more of the higher components.

Except for the indirect evidence of Gault & Boisselet,[61] who stated that the melting point of a mixture of waxes may be calculated by the rule of mixtures i.e. the melting point of the mixtures lies between the melting points of the components, the idea of solid solution formation remained unconfirmed by experiment until the work of Myers & Stegeman[62] who investigated the equilibria existing in mixtures of waxes of different melting points. By repeated carefully controlled fractionations under 0·1 m.m. pressure of a large quantity of wax, and the ultimate collection of fractions boiling over a narrow range, waxes of different melting points were obtained. The four fractions selected for the experiments had the following boiling ranges (under 0·1 m.m.)

A - 165 - 169°C.

B - 185 - 188°C.

C - 150 - 155°C.

D - 205 - 210°C.

A series of mixtures of different proportions of wax A and wax B were prepared. The mixtures were melted in a large test tube and allowed to cool slowly. The temperatures at which crystals appeared in the melts were readily ascertained and, being characteristic of each mixture, furnished the data from which the upper curve in Fig. I was constructed.

The temperature at which solidification was complete was ascertained from a study of the cooling curve of each wax mixture. From the results obtained, the lower curve of Fig. I was plotted. A similar series of measurements on mixtures of waxes C. and D. gave curves (Fig. 2) of similar characteristics.

These authors suggest that the nature of the relationships indicated in Figs. 1 and 2 provide evidence that wax mixtures form a complete series of solid solutions, the freezing points of which lie between the freezing points of the components.

More recently,[63] a study has been made of the melting curves of pure n-paraffins and commercial waxes, and it is suggested that the behaviour of the commercial waxes may be explained as being that of a mixture of solid solutions of substances which have two enantiotropically related modifications.

The original theoretical ideas of Gurwitsch have therefore received adequate experimental support, and it is logical that any attempt to construct an equilibrium diagram that is applicable to the process of sweating, or more correctly, in the case of waxes which contain no oil - fractional melting - should be developed from the basis indicated by the consideration that paraffin wax consists of a series of solid solutions - probably of n-paraffins. Various

types of equilibrium diagrams for solid solutions are described in the literature, but in view of the observation of Gault & Boisselet and the findings of Myers & Stegeman, to which reference has already been made, any diagram applicable to the process of fractional melting of waxes is more likely to resemble that for a continuous series of solid solutions rather than those in which minimum or maximum melting solid solutions are formed. It is essential, therefore, to make a brief study of a typical equilibrium diagram of this nature.

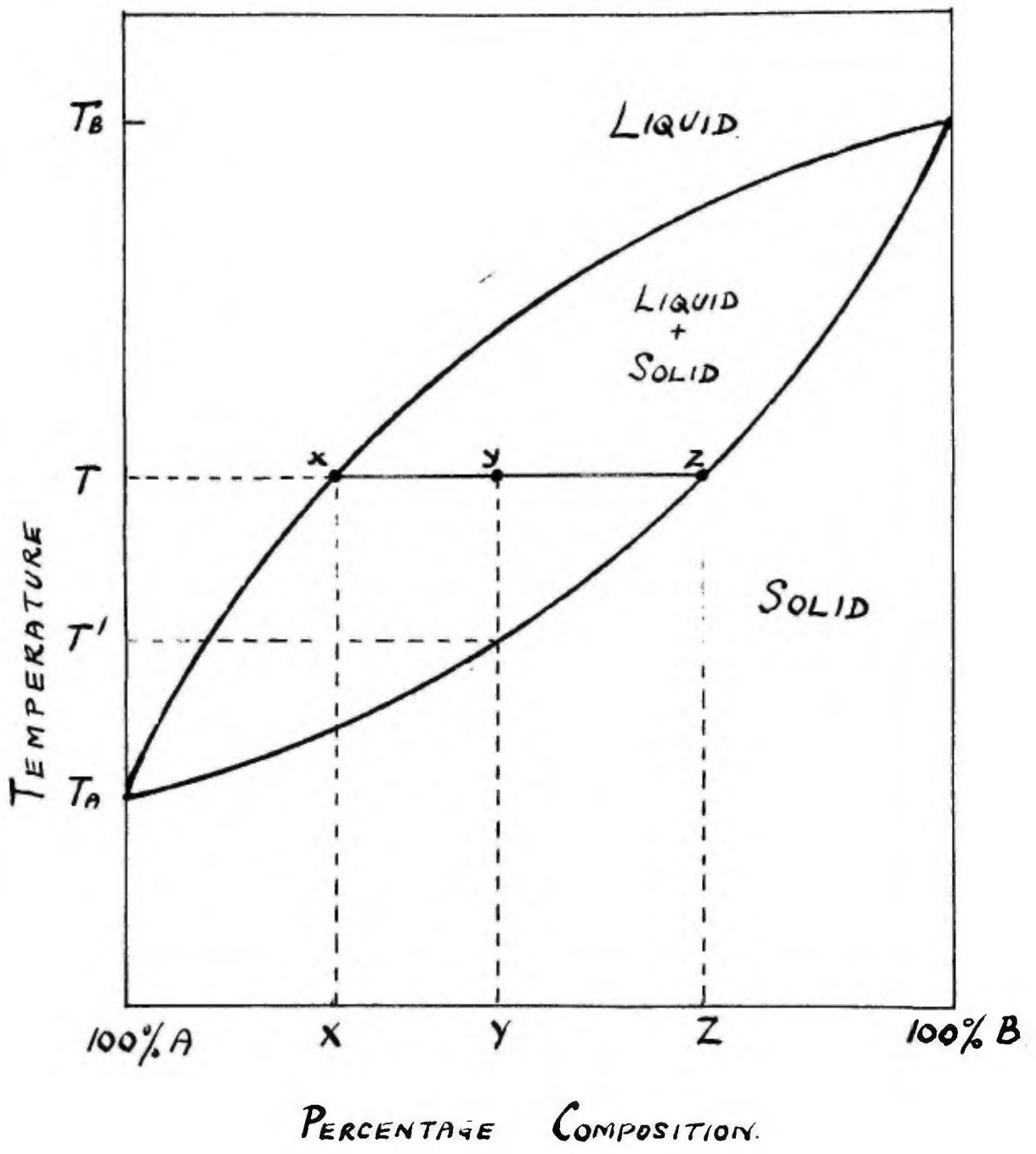

T_B
LIQUID
LIQUID
+
SOLID
x
y
z
T
T'
T_A
SOLID
TEMPERATURE
100% A
X
Y
Z
100% B
PERCENTAGE COMPOSITION.

FIG. 3.

Substances forming a Continuous Series of Solid Solutions - Study of Equilibrium Diagram.

Figure 3 is a typical equilibrium diagram for two substances A. and B. which melt respectively at temperatures T_A and T_B.

The upper curve is the "liquidus" or equilibrium curve of the liquid solution and the lower curve is the "solidus" or equilibrium curve of the solid solution formed by these substances. Any system represented by a point in the region above the liquidus curve is entirely liquid and in the region below the solidus curve is entirely solid. Any system represented by a point in the region between the solidus and the liquidus curves is partly liquid and partly solid, the relative amount of each phase present being calculated in the following manner :-

Consider a mixture (Fig. 3) of A. and B. of composition Y, i.e. having Y%B and (100 - Y)%A, and assume equilibrium to be attained at a temperature T. Mixture Y separates into a liquid phase x of composition X and a solid phase z of composition Z.

Let there be (a) grams of liquid phase and (b) grams of solid phase. Then total amount of Y taken is (a + b) grams, and obviously Y contains $\frac{Y}{100}$ (a + b) grams of B and $\frac{(100-Y)}{100} \times (a+b)$ grams of A.

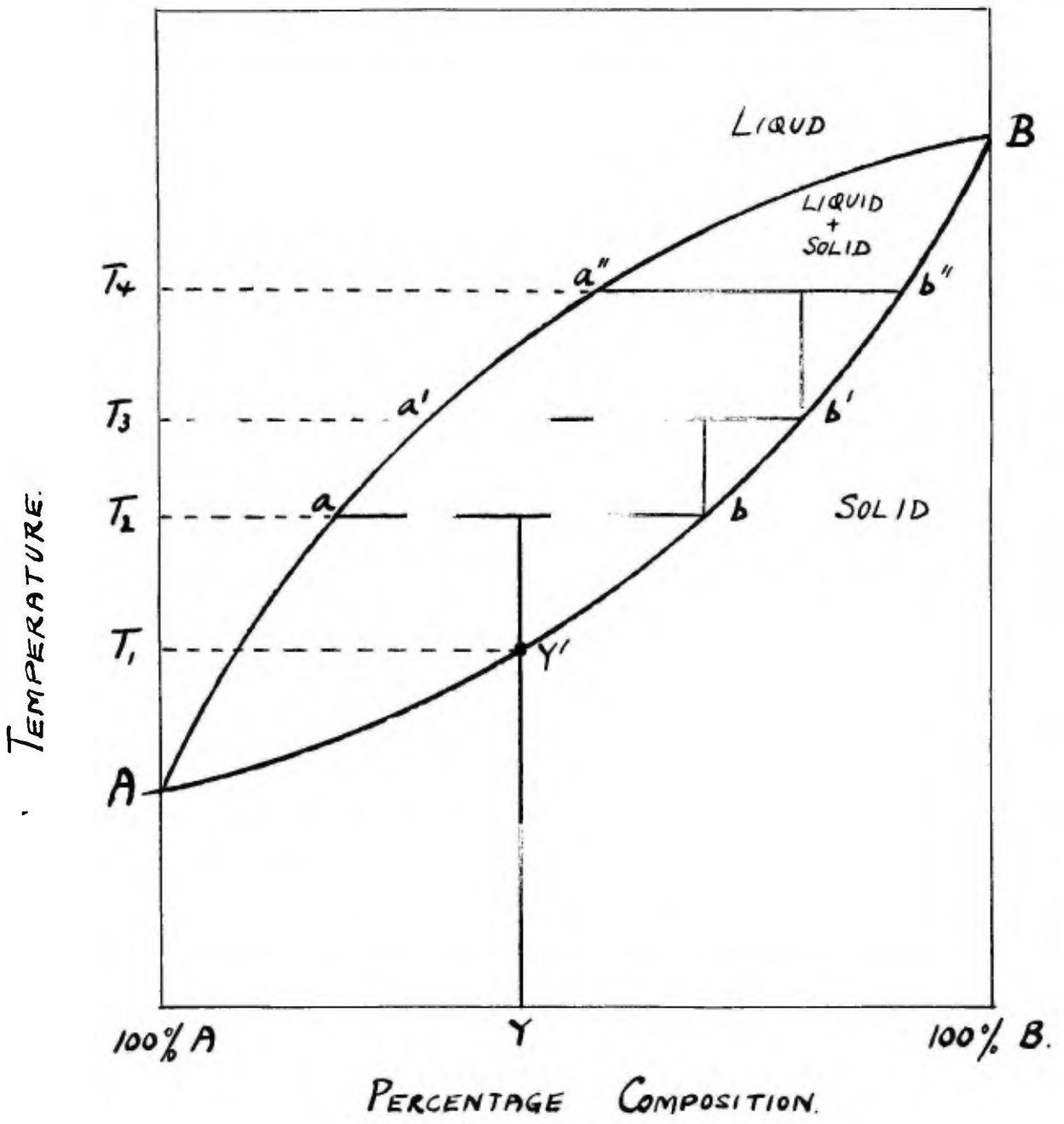

LIQUID
B
LIQUID
+
SOLID
T_4
a''
b''
T_3
a'
b'
T_2
a
b
SOLID
T_1
Y'
A
TEMPERATURE.
100% A
Y
100% B.
PERCENTAGE COMPOSITION.

FIG. 4

Now (a) grams of X contain $\left(a \times \frac{X}{100}\right)$ grams of B.

and (b) grams of Z contain $\left(b \times \frac{Z}{100}\right)$ grams of B.

Hence $\frac{Y}{100}(a + b) = \frac{aX}{100} + \frac{bZ}{100}$

i.e. $a(Y-X) = b(Z-Y)$

i.e. $\frac{a}{b} = \frac{(Z-Y)}{(Y-X)}$ ----------(Equation 1(a).)

from which the relative amounts of liquid and solid phases may be calculated.

Consider now the effect of slowly heating a mixture of composition Y (Figure 4). No phase change occurs until temperature T_1 is reached, at which stage liquid appears. At T_2, liquid of composition (a) exists in equilibrium with solid of composition (b). Let the liquid phase be completely removed and let the remaining solid phase reach equilibrium at temperature T_3, where the liquid phase is of composition (a') and the solid phase is of composition (b'). Again completely remove the liquid phase and let the remaining solid phase reach equilibrium at T_4, where the compositions of liquid and solid phases are (a") and (b") respectively.

Thus, in this particular 3-stage removal of liquid phase, the composition of the solid phase changes from Y to (b"), and the yield of (b") may be calculated as indicated on the previous page.

If, therefore, solid of composition Y is taken at

temperature $T_{\frac{1}{2}}$ and subjected to an infinitely large number of infinitesimally small temperature increments and the resulting liquid phase is removed from the solid after each temperature increase, it follows that the composition of the solid remaining will change from Y' to B along the curve Y'B. In this ideal process pure B, the higher melting component will therefore ultimately be obtained, but in almost zero yield.

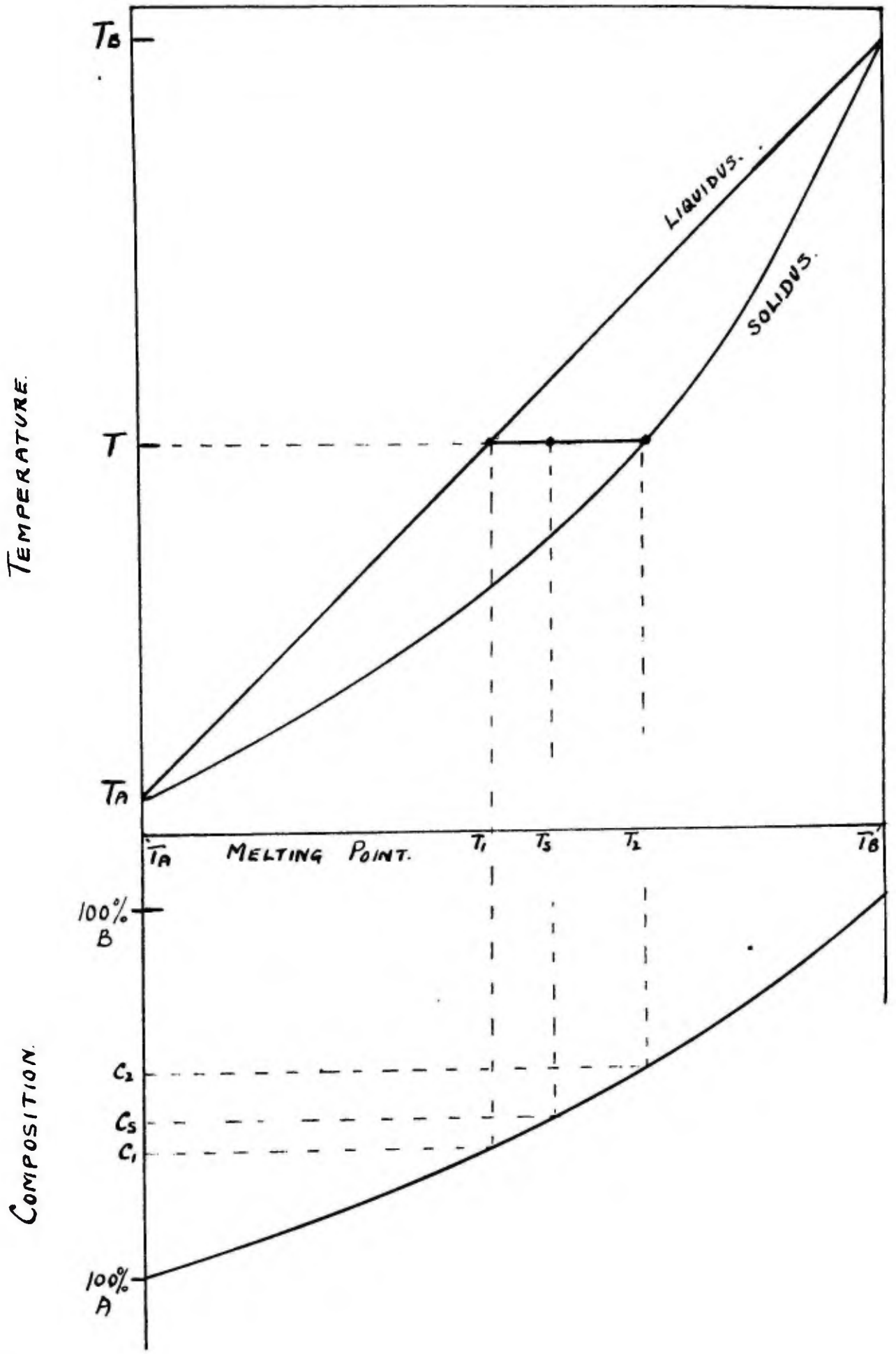

TEMPERATURE.
T_B
T
T_A
LIQUIDUS.
SOLIDUS.
T_A
MELTING POINT.
T_1
T_3
T_2
T_B
100% B
COMPOSITION.
C_2
C_3
C_1
100% A

FIG. 5.

Modified Representation of Equilibrium Diagram for a Continuous Series of Solid Solutions.

The equilibrium diagram for two substances forming a continuous series of solid solutions has been given in the usual and simplest form in Fig. 4 (Page 18a). It is clear, however, that it may also be represented in the somewhat more complicated form shown in Fig. 5 opposite. In this diagram, Equilibrium Temperature is plotted against melting point, defined in this case as that temperature at which solid first appears on cooling a liquid containing any proportions of components A and B. It follows from Fig. 4 (Page 18a) that the property of melting point is not additive, and the curve showing melting point versus composition is also shown in Fig. 5 so that computations may be evolved in a manner similar to that indicated in the previous pages.

The liquidus curve is obviously a 45° line as the melting point of the liquid phase formed by any mixture at a temperature such that it falls within the liquidus-solidus region, is the same as the equilibrium temperature (Fig. 4). The solidus curve in Fig. 5 may easily be obtained by re-plotting the data from Fig. 4.

Applying the theory developed in the previous pages to this modified equilibrium diagram, it follows that if a mixture of the two components of melting point T_S, and therefore composition C_S, is allowed to reach equilibrium at a temperature

T and then separated completely into the two phases, the liquid phase will be of melting point T_1 and composition C_1, whilst the solid phase will be of melting point T_2 and composition C_2. Also, from Equation 1(a) (Page 18) the ratio

$$\frac{\text{Liquid phase}}{\text{Solid phase}} = \frac{C_2 - C_S}{C_S - C_1}.$$

If melting point in any particular case happened to be additive, i.e. directly proportional to the amounts of the two components in the mixture, it is obvious that for purposes of computation the lower curve (Fig. 5) showing melting point versus composition would be unnecessary, as the relative amounts of the liquid and solid phases would be given by $(T_2 - T_S)$ and $(T_S - T_1)$ respectively. In such a case, the upper curve of Fig. 4 would become a straight line.

The significance of this modified equilibrium diagram will become apparent in a later section when the actual equilibrium diagram for mixtures of waxes is considered.

Preliminary Experiments on Wax/Oil and Wax Mixtures.

Experiments of a preliminary nature designed to give some indication of the form of the equilibrium diagram desired, were performed on the following samples :-

(A) Anglo-Iranian Slack-Wax ex Llandarcy Refinery

(B) De-oiled Anglo-Iranian Slack-Wax prepared from the Slack-Wax (A)

(C) Blends of commercial waxes.

The reason for experiments on the above three different classes of stock will become apparent later in this section when it will be shown that the use of stock (B) is a logical development from the results obtained with stock (A). Similarly, for stock (C) with reference to stock (B).

It has already been stated that two general methods may be employed to determine the equilibrium diagrams given by substances forming solid solutions :-

(a) Thermal analysis - a method based on the determination of melting and solidification points for mixtures of known composition; from the study of heating or cooling curves; or by direct observation of the beginning and end of melting,

and (b) Allowing a suitable mixture to attain equilibrium at a temperature within the melting range of the components, completely separating the liquid from the solid phase, and then analysing the two phases.

The first method was used by Myers and Stegeman in the experiments already briefly described (Page /4), but these workers were dealing with two very close-cut fractions, each melting over a range of not more than 1°C. and which were assumed to be pure compounds. Thus the actual determination of the melting and solidification points of known mixtures was possible. This method obviously cannot be applied to mixtures of waxes containing unknown quantities of many components, and it was therefore necessary to resort to method (b) above.

Use of Cloud Point for Characterising Liquid and Solid Phase Fractions.

A difficulty is immediately encountered here as the composition of the wax is unknown and it is therefore necessary to employ some property, for example cloud point, melting point, molecular weight, etc. to indicate the difference between the liquid and solid phases formed in the equilibrium experiments. For this preliminary work it was decided to use the property of "cloud point" which may be determined easily and conveniently as described below. It should be mentioned at this stage that the property of melting point was used instead of cloud point in the main work. The reasons for the choice are discussed at some length in a later section (Page 54).

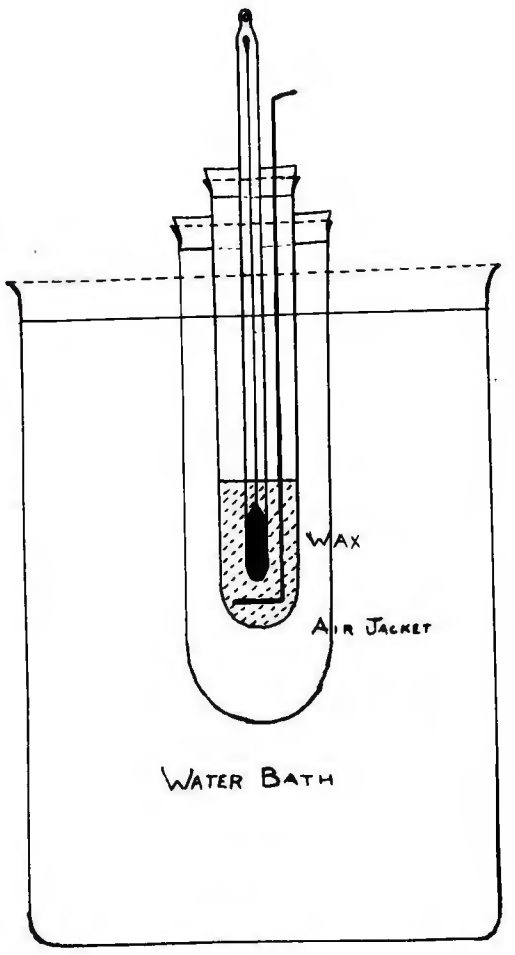


FIG. 6.

Cloud Point Determination:- An ordinary 8" test-tube was filled to a mark ($1\frac{1}{2}$" from bottom) with the wax or oil-wax mixture, and placed in an air-jacket of slightly larger dimensions. This, in turn, was placed in a 3-litre beaker containing water at a temperature 10-15°F. lower than the expected cloud-point of the sample. An N.P.L. Standard I.P.T. Wax Melting-Point Thermometer was placed in the molten sample, thus giving a set-up as illustrated in Fig. 6.

The sample was allowed to cool with regular stirring until solid showed signs of appearing. Vigorous stirring was then commenced and continued until a "cloud" effect appeared in the sample. The temperature at which this effect was observed was designated as "cloud-point". Results were reproducible within 0·2°F. in the case of wax and wax-oil mixtures, and this margin of error was considered satisfactory for the preliminary experiments.

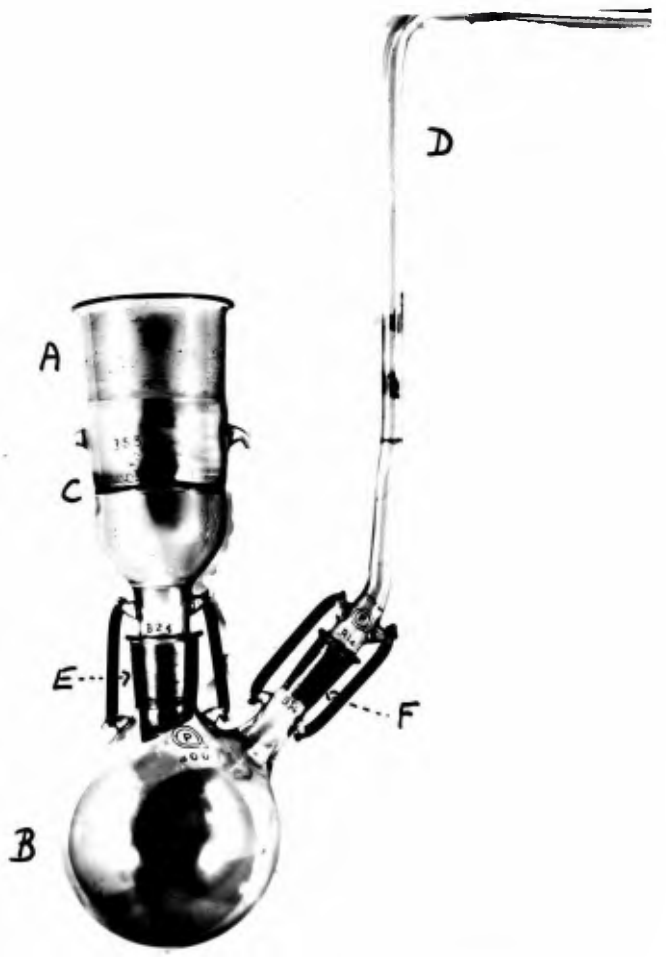


FIG. 7.

Apparatus for Separating liquid from solid phase wax in Equilibrium Experiments

The apparatus used in these preliminary experiments for the separation of the liquid from the solid phase wax is illustrated in Fig. 7 opposite.

The entire piece of apparatus was constructed of glass and each section was connected by means of a ground glass joint. The whole apparatus was immersed in the Thermostat at the required equilibrium temperature to within ½" of the top of Flask A. The wax sample was also allowed to stand in the Thermostat, but was contained in a wide boiling tube of convenient length. The wax sample was allowed to reach equilibrium over a period of four hours, during which time it was constantly stirred. At the end of this period the sample was very quickly transferred to Flask A. in which the perforated glass disc C was covered with a filter paper. The sample was allowed to stand a further 15 minutes in this condition, after which time suction was applied through the tube D.

Suction was continued for as long as necessary - normally for two hours, but depending on the amount of solid phase present - the greater the amount of solid, the longer was the suction continued.

When no more liquid phase was dropping from Flask A, the solid phase remaining was covered with pieces of filter paper which were pressed in to the wax with a small metal plunger. This process was continued until no wax stain appeared on the filter paper after pressing.

The apparatus was then removed from the Thermostat and disconnected at the ground-glass joints E and F. Flask B was weighed before and after the experiment and the weight of liquid phase obtained by difference, after correcting for the amount removed by pressing the solid phase with filter paper.

The solid phase was removed from Flask A and weighed.

The cloud points were found for both the solid and liquid phases.

Thermostat. The Thermostat, which was of 10 gallons capacity, was of the normal electrically controlled type with mercury cut-out, toluene-mercury regulator, and the usual accessories, including an efficient electrically controlled stirrer, constant level device, etc. With special care being given to maintaining the mercury at the top of the regulator in a clean condition, the Thermostat could be controlled to $0{\cdot}01^{\circ}C$. but it was not considered necessary to maintain such accuracy, and the temperature was therefore controlled to $\pm 0{\cdot}05^{\circ}C$, this degree of accuracy being attained without undue attention being given to the regulator.

The results of equilibrium experiments with the three different stocks are now described.

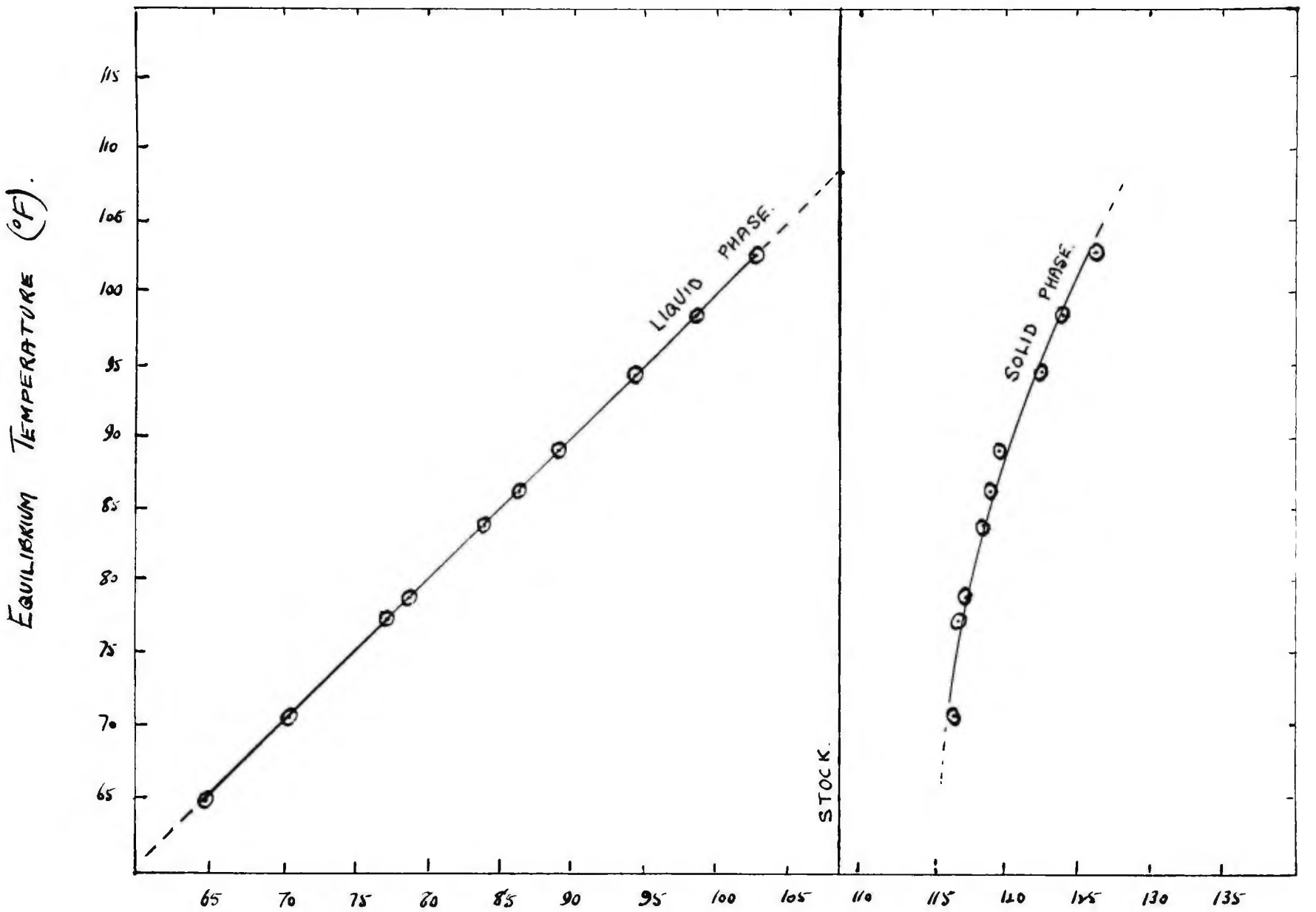

EQUILIBRIUM TEMPERATURE (°F).
115
110
105
100
95
90
85
80
75
70
65
LIQUID PHASE.
SOLID PHASE.
STOCK.
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
CLOUD POINT (°F).

FIG. 8.

(A) Anglo-Iranian Slack Wax

This Slack-wax, which from its appearance obviously contained a large amount of oil, had a Cloud-Point of 108·7°F. and a Melting-Point (as determined by the A.S.T.M. Method - Serial Designation - D.87-22) of 108·0°F. Equilibrium experiments were conducted over the temperature range 70·7°F. to 102·8°F. in the apparatus and in the manner previously described. In each experiment the yields and cloud-points of the solid and liquid phases were determined. Results are given in Table II below :-

TABLE II

		% by Weight		Cloud Point	
Experiment	Equilibrium Temp.	Solid Phase	Liquid Phase	Solid Phase	Liquid Phase
1	70.8	72.6	27.4	116.5	70.7
2	77.7	66.3	33.7	117.1	77.5
3	79.2	66.9	33.1	117.2	79.0
4	80.3	65.4	34.6	117.6	80.2.
5	84.1	62.7	37.3	118.5	84.0
6	86.7	59.2	40.8	119.1	86.5
7	89.4	55.7	44.3	119.7	89.2
8	92.2	49.8	51.2	120.9	92.0
9	94.6	43.2	56.8	122.5	94.5
10	99.1	31.8	68.2	124.2	99.0
11	102.9	19.6	80.4	126.2	102.8

These results are represented graphically in Fig. 8 opposite.

It will be noted from the figures given in Table II that the cloud-point of the liquid phase is in all cases not more than $0{\cdot}3^{\circ}F.$ lower than the equilibrium temperature. This was to be expected from the method of determining cloud-point, as the liquid phase may be considered as a liquid saturated with solid at the equilibrium temperature, and it is therefore obvious that when a sample is cooled (with stirring, to prevent any supersaturation effect) solid will be deposited at a temperature slightly lower than that at which the liquid phase was removed from the solid with which it was in equilibrium.

On the <u>assumption</u> that cloud-point for oil/wax mixtures is an additive property, the yields of each phase could be calculated from a knowledge of the cloud-points of the liquid and solid phases and the stock, as follows :-

$$\text{Solid phase} = \frac{C - C_L}{C_S - C_L} \times 100 \ \%$$

$$\text{Liquid phase} = \frac{C_S - C}{C_S - C_L} \times 100 \ \%$$

where C, C_L, and C_S represent the cloud-points of the stock, liquid, and solid phases respectively. Using this relation, the yield of solid phase was calculated for each of the eleven experiments given in Table II. Experimental and calculated values are given in Table III, as follows :-

TABLE III

Expt.	Equilibrium Temp.	% Yield of Solid Phase		
		Experimental	Calculated	Experimental - Calculated
1.	70.8	72.6	83.0	- 11.4%
2.	77.7	66.3	78.8	- 12.5%
3.	79.2	66.9	77.8	- 10.9%
4.	80.3	65.4	76.2	- 10.8%
5.	84.1	62.7	71.6	- 8.9%
6.	86.7	59.2	68.1	- 8.9%
7.	89.4	55.7	63.9	- 8.2%
8.	92.2	49.8	57.8	- 8.0%
9.	94.6	43.2	50.7	- 7.5%
10.	99.1	31.8	38.5	- 7.3%
11.	102.9	19.6	25.2	- 5.6%

Agreement between the experimental and calculated values is poor and the discrepancy must be due to the cloud-point not being an additive property for oil-wax mixtures. The non-additivity of the relation was demonstrated by determining the cloud-points of various blends of an oil/wax mixture of cloud-point 69.6°F. and a wax of cloud-point 132.2°F., both having been extracted from the Anglo-Iranian Slack Wax. Table IV as follows, gives the cloud-points of various blends :-

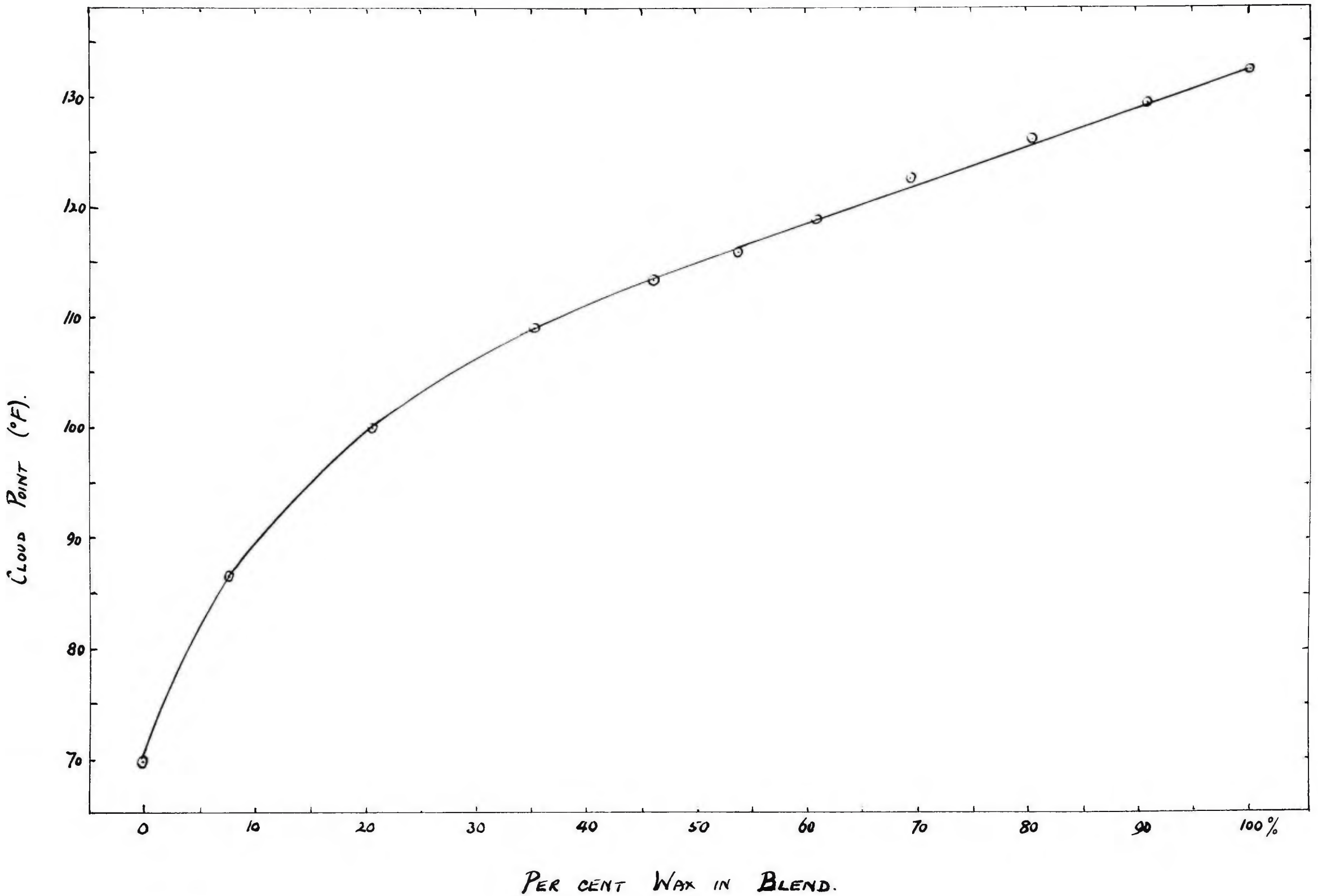

Cloud Point (°F).
130
120
110
100
90
80
70
0
10
20
30
40
50
60
70
80
90
100%
Per cent Wax in Blend.

FIG. 9.

TABLE IV

% Wax (C.P.132.2°F.)	% Oil (C.P.69.6°)	Cloud Point °F.
100	0	132.2
90.8	9.2	129.3
80.6	19.4	125.9
69.5	30.5	122.3
60.8	39.2	118.8
53.7	46.3	115.8
46.1	53.9	113.3
35.4	64.6	108.8
20.7	79.3	99.8
7.8	92.2	86.2
0	100	69.6

These results are shown graphically in Fig. 9. and indicate that for mixtures containing more than 40% wax, the cloud-point is a linear function of the amount of wax added. For smaller amounts of wax in the blend, the cloud-point/composition relation is a curve, the steepness of which depends on the cloud-point of the oil/wax constituent. Incidentally, the graph confirms observations by other workers that the solubility of wax in oil shows a marked increase at temperatures approximately 20°F. below the cloud-point of the wax.

Solid Phase obtained in Two-Stage Separation.

For substances forming a continuous series of solid solutions it is easily seen from Fig. 3 (Page 17a) that for a mixture of composition Y, for example, no matter whether the liquid phase is removed in any number of stages between temperature T^1 and T, provided that the final separation of liquid from solid phase takes place at temperature T, the composition of the solid phase will always be Z. The yield of this solid will, of course, depend on the number and nature of the stages. It was therefore decided to ascertain whether the equilibrium diagram obtained for the slack-wax applied to a two or more stage process.

Three experiments were performed, the results of which are given below :-

Experiment (a).

The slack-wax stock of Cloud-point 108.7°F. was allowed to reach equilibrium in the usual manner at a temperature of 86.7°F. The two phases were separated and the cloud-point was determined for each phase: (Expt. 6 - Table 2), with the following results :-

Equilibrium Temp. 86.7°F.

Liquid Phase: Yield 40.8% Cloud-Point 86.5°F.

Solid Phase: Yield 59.2% Cloud-Point 119.1°F.

The solid phase obtained in this experiment was then allowed to attain equilibrium at a temperature of 99.2°F. and the usual

procedure followed for the removal of the liquid phase. Results were as follows :-

Equilibrium Temperature 99.2°F.

Solid Phase: Yield 84.4% (Equivalent to 84.4 x $\frac{59.2}{100}$ %
= 49.4% on original stock)
Cloud-Point = 121.4°F.

Liquid Phase: Yield 15.6% (Equivalent to 15.6 x $\frac{59.2}{100}$ %
= 9.2% on original stock)
Cloud-Point 99.1°F.

Thus, successive removals of the liquid phase from the Anglo-Iranian Slack Wax at two different temperatures, 86.7°F. and 99.3°F, resulted in the following products :-

Yield Summary for the Two-Stage Process.

Final Equilibrium Temperature = 99.3°F.

40.8% Liquid Phase of Cloud-Point 86.5°F.

9.2% Liquid Phase of Cloud-Point 99.1°F.

49.9% Solid Phase of Cloud-Point 121.4°F.

It will be noted, however, (Expt. 10. Table II), that a one-stage removal of liquid from solid phase at a temperature of 99.1°F. results in a 31.8% yield of solid phase of Cloud-Point 124.2°F. The two-stage removal of liquid phase therefore results in a higher yield of wax of lower cloud-point than that obtained in a one-stage removal at the same final equilibrium temperature. (The slight difference -0.2°F. - between the final equilibrium temperatures in the above comparison is immaterial).

It will also be seen from Fig. 8 that a solid phase of cloud-point 121.4°F. is obtained by a one-stage separation of liquid from solid phase at a temperature of 92.8°F. (approximately) in yield, estimated from the figures in Table II, of 47 - 48%.

Experiment (b).

A second experiment similar to (a) above was performed, the two equilibrium temperatures being 77.7°F. and 99.3°F. The usual procedure was followed, and the following is a summary of the results :-

1st Equilibrium Temperature 77.7°F.
Liquid Phase: Yield 33.7% Cloud-Point 77.5°F.
Solid Phase: Yield 66.3% Cloud-Point 117.2°F.

2nd Equilibrium Temperature 99.3°F.
Liquid Phase: Yield 18.0% Cloud-Point 99.0°F.
Solid Phase: Yield 82.0% Cloud-Point 121.0°F.

Yield Summary for the Two-Stage Process.

Final Equilibrium Temperature 99.3°F.
33.7% Liquid Phase of Cloud-Point 77.5°F.
11.9% Liquid Phase of Cloud-Point 99.0°F.
54.4% Solid Phase of Cloud-Point 121.0°F.

It will be noted that in this experiment too, the removal of the liquid phase at two different temperatures results in a higher yield of solid phase of lower cloud-point than that obtained in

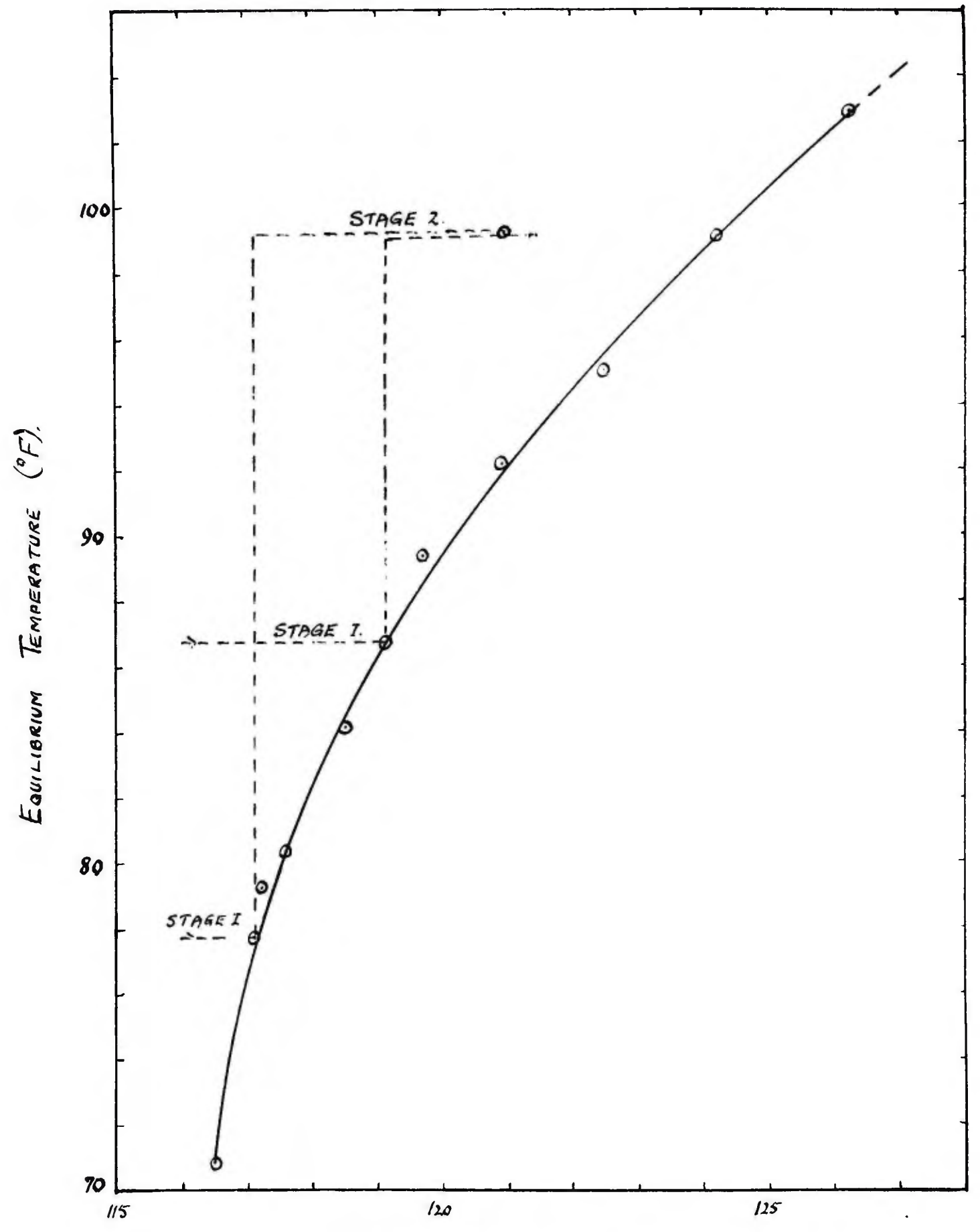

STAGE 2.
STAGE 1.
STAGE I
100
90
80
70
115
120
125
EQUILIBRIUM TEMPERATURE (°F).
CLOUD POINT OF SOLID PHASE (°F).

FIG. 10.

a one-stage removal at the same final equilibrium temperature. Also, it is seen from Fig. 8 that a solid phase of cloud-point 121.0°F. is obtained by a one-stage separation at a temperature of 91.9°F. in yield (estimated from Table II) of 49 - 50%. The findings of these two experiments are illustrated in Fig. 10, in which cloud-point of the solid phase is plotted against the equilibrium temperature.

Experiment (c).

A third experiment of a similar nature was performed on the liquid phase obtained from an equilibrium experiment at 102.9°F. (Expt. 11. Table II). This liquid was allowed to attain equilibrium at 80.3°F., and the two phases were then separated in the usual manner. Results were as follows :-

1st Equilibrium Temperature 102.9°F.

Solid Phase: Yield 19.6% Cloud-Point 126.2°F.

Liquid Phase: Yield 80.4% Cloud-Point 102.8°F.

2nd Equilibrium Temperature 80.3°F.

Solid Phase: Yield 55.6% Cloud-Point 114.2°F.

Liquid Phase: Yield 44.4% Cloud-Point 80.2°F.

Yield Summary for the Two-Stage Process.

Final Equilibrium Temperature 80.3°F.

19.6% Solid Phase of Cloud-Point 126.2°F.

44.7% Solid Phase of Cloud-Point 114.2°F.

35.7% Liquid Phase of Cloud-Point 80.2°F.

The yield and cloud-point of the liquid phase obtained after the second separation at 80.3°F. are - within experimental error - the same as for the liquid phase obtained in the one-stage separation at 80.3°F. (See Expt. 4. Table II).
The solid phase obtained in this second stage is, however, of cloud-point considerably lower than that obtained in the one-stage process (Expt. 4. Table II).

Interpretation of Results.

(1) Using the property of cloud-point to characterise the liquid and solid phases obtained in experiments (a) and (b), it is shown that for a given final equilibrium temperature T, the removal of the liquid phase in equilibrium with solid in two stages - at temperatures T^1 and T ($T > T^1$) results in a higher yield of solid phase of lower cloud-point that that obtained by the one-stage removal of the liquid phase at T.

This observation may be explained in terms of the solubility of ~~oil~~ wax in ~~wax~~ oil. It is known that the solubility of ~~oil~~ wax in ~~wax~~ oil.

(a) increases with increase in temperature, and

(b) decreases with increase in the melting-point (and therefore the cloud-point) of the wax.

Consider then, the liquid removed at T^1. This liquid is a saturated solution of wax in oil at temperature T^1. In the second-stage removal at T ($T > T^1$) the liquid removed is saturated with wax at this higher temperature. Suppose now that the solid remaining after this second removal of liquid is added to the liquid removed at the lower temperature T^1. At the higher temperature T, this liquid is not saturated with respect to the solid, and therefore more solid will dissolve until the liquid becomes saturated at temperature T. The constituents of lower melting-point (or cloud-point) will be dissolved preferentially and the solid remaining will therefore have a higher

cloud-point than that remaining after the first extraction at this temperature T. The results of Expt. (c) may be explained by similar considerations.

On this reasoning, then, the solid remaining after a two- (or more) stage removal of liquid in the manner described will always have a lower cloud-point than that obtained in a one-stage removal at the higher (or highest) equilibrium temperature, as observed in these experiments.

(2) As the property of cloud-point, and incidentally melting-point, is not additive for oil-wax mixtures, any equilibrium diagram obtained could not be used to calculate the yields of liquid and solid phases. Various artifices were tried in an effort to obtain an equilibrium diagram of the form of Fig. 8 on a quantitative basis, but as these attempts were unsuccessful they will not be described.

Thus, in an endeavour to simplify the problem it was decided to remove the oil and to perform similar equilibrium experiments using de-oiled Anglo-Iranian Slack Wax.

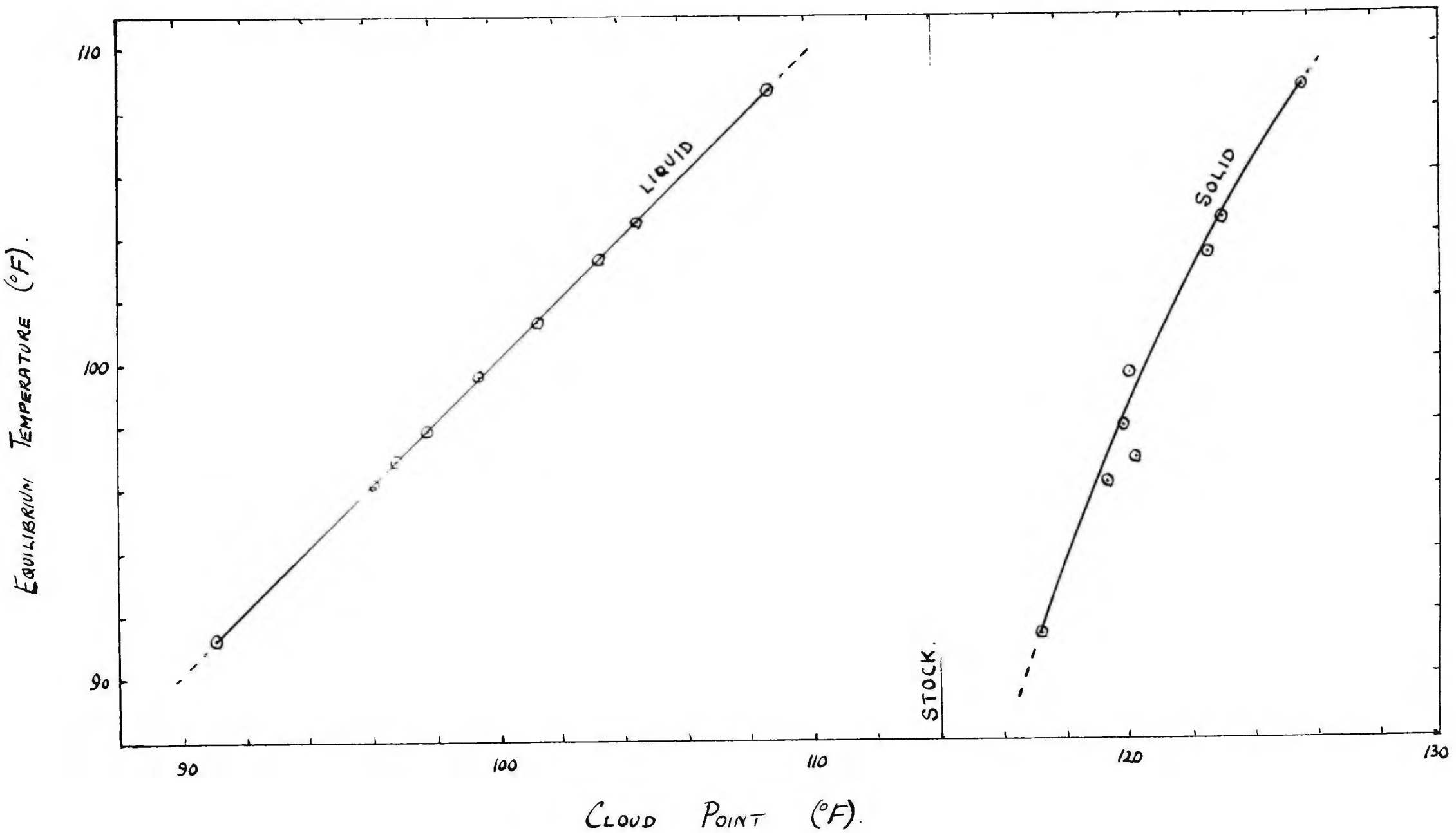

EQUILIBRIUM TEMPERATURE (°F).
110
100
90
LIQUID
SOLID
STOCK.
90
100
110
120
130
CLOUD POINT (°F).

FIG. 11.

(B) De-oiled Anglo-Iranian Slack Wax.

The slack-wax stock used in the previous experiments was three times extracted with acetone at room temperature and pressed after each extraction. Final traces of solvent were removed by distilling under reduced pressure in a current of nitrogen. The de-oiled stock thus obtained had a cloud-point of 114.0°F. The equilibrium diagram was obtained in the same manner as for the Anglo-Iranian Slack Wax. Yields and cloud-points of the liquid and solid phases were obtained over the temperature range 91.3° to 108.7°F. with the results shown in Table V. below :-

TABLE V.

Experiment	Equilibrium Temperature	% by Weight		Cloud Point	
		Solid Phase	Liquid Phase	Solid Phase	Liquid Phase
1.	91.3	89.1	10.9	117.2	91.0
2.	96.1	78.2	21.8	119.3	96.0
3.	97.9	75.6	24.4	119.8	97.7
4.	99.6	72.1	27.9	120.0	99.3
5.	103.4	58.1	41.9	122.5	103.2
6.	104.5	54.5	45.5	123.0	104.3
7.	108.7	33.2	66.8	125.7	108.6
8.	96.9	72.4	27.6	120.2	96.7

These results are represented graphically in Fig. 11 opposite.

It will be noted that the cloud-point of the solid phase obtained in Experiment 8 is 0.7°F. higher than expected

from the curve given by drawing through the other points. In this particular experiment extra precautions were taken to separate the liquid from the solid phase. The sample was allowed to reach equilibrium by remaining in the thermostat for 24 hours before transfer to the filtration apparatus, where it was allowed to stand for another six hours before commencing filtration. As much of the liquid phase as possible was removed during the first period of filtration. The sample was allowed to remain in the thermostat for a further 48 hours during which time filtration was intermittent. At the end of this period the apparatus was removed from the thermostat and the amount and cloud-point of each phase determined. The yield of solid phase is normal for its cloud-point. This particular experiment suggests that the method employed for the separation of the two phases may be unsatisfactory, and this will later be considered in more detail.

On the assumption that cloud-point is additive for a de-oiled wax, the yield of solid was calculated-in the manner given previously (Page 28)-for each of the eight equilibrium experiments given in Table V. Experimental and calculated values are given in Table VI as follows :-

TABLE VI.

Expt.	Equilibrium Temperature	% Yield - Solid Phase		
		Experimental	Calculated	Experimental - Calculated
1.	91.3	89.1	87.8	+ 1.3%
2.	96.1	78.2	77.3	+ 0.9%
3.	97.9	75.6	73.8	+ 1.8%
4.	99.6	72.1	71.0	+ 1.1%
5.	103.3	58.1	55.9	+ 2.2%
6.	104.5	54.5	51.9	+ 2.6%
7.	108.7	33.2	31.6	+ 1.6%
8.	96.9	72.4	73.6	- 1.2%

Agreement between experimental and calculated yields is fairly good; in the first seven experiments the calculated figure is, on an average, only 1.5% higher than the experimental

Solid Phase obtained in Two-Stage Separation.

The main object of the experiments with de-oiled Slack Wax was to determine the effect of liquid removal at two different temperatures on the cloud-point of the solid obtained after the second removal of liquid. Accordingly, the solid phase resulting from Experiments 1, 2, 3 and 8 (Table V.) was in each case allowed to reach equilibrium at a higher temperature, after which the liquid phase was removed in the usual manner. The results of the four two-stage experiments are summarised below :-

Expt. 1(a) - Solid Phase ex Expt. 1. Table V.

	Equil. Temp.	% by Weight Solid Phase	% by Weight Liquid Phase	Cloud-Point Solid Phase	Cloud-Point Liquid Phase
1st Stage (Expt.1. Table V).	91.3	89.1	10.9	117.2	91.0
2nd Stage	103.5	77.6	22.4	120.6	103.4

Yield Summary for the Two-Stage Process

Final equilibrium temperature 103.5°F.

10.9% Liquid Phase of Cloud-Point 91.0°F.

20.1% Liquid Phase of Cloud-Point 103.4°F.

69.0% Solid Phase of Cloud-Point 120.6°F.

It will be noted from Table V. (Expt. 5) that a one-stage removal of liquid phase at an equilibrium temperature of

103.4°F. results in a 58.1% yield of solid phase of cloud-point 132.5°F. In this case, therefore, the two-stage removal results in a higher yield of lower cloud-point solid phase than that obtained in a one-stage separation of liquid from solid at the higher equilibrium temperature.

Similar results are obtained in the other two-stage experiments as shown below :-

Expt. 2 (a) - Solid Phase ex Expt. 2. - Table V.

	Equil. Temp.	% by Weight Solid Phase	% by Weight Liquid Phase	Cloud-Point Solid Phase	Cloud-Point Liquid Phase
1st Stage (Expt.2. Table V)	96.1	78.2	21.8	119.3	96.0
2nd Stage	104.9	85.4	14.6	121.6	104.6

Yield Summary

21.8% Liquid Phase of Cloud-Point 96.0°F.

11.4% Liquid Phase of Cloud-Point 104.6°F.

66.8% Solid Phase of Cloud-Point 121.6°F.

Expt. 3 (a) - Solid Phase ex Expt. 3. - Table V.

	Equil. Temp.	% by Weight Solid Phase	% by Weight Liquid Phase	Cloud-Point Solid Phase	Cloud-Point Liquid Phase
1st Stage (Expt.3. Table V)	97.9	75.6	24.4	119.8	97.7
2nd Stage	104.5	88.7	11.3	121.4	104.2

Yield Summary

24.4% Liquid Phase of Cloud-Point 97.7°F.

8.6% Liquid Phase of Cloud-Point 104.2°F.

67.0% Solid Phase of Cloud-Point 121.4°F.

Expt. 8 (a) - Solid Phase ex Expt. 8. - Table V.

	Equil. Temp.	% by Weight Solid Phase	% by Weight Liquid Phase	Cloud-Point Solid Phase	Cloud-Point Liquid Phase
1st Stage (Expt.8. Table V)	96.9	72.4	27.6	120.2	96.7
2nd Stage	104.9	90.1	9.9	121.2	104.6

Yield Summary

27.6% Liquid Phase of Cloud-Point 96.7°F.

7.2% Liquid Phase of Cloud-Point 104.6°F.

65.2% Solid Phase of Cloud-Point 121.2°F.

The final solid phase obtained in each of the experiments 2(a), 3(a), and 8(a) may be compared with the solid phase obtained in a one-stage removal at an equilibrium temperature of 104.5°F. (Expt. 6. Table V.) in which a 54.5% yield of solid of cloud-point 123.0°F. was obtained.

It is apparent from these experiments that a two-stage process

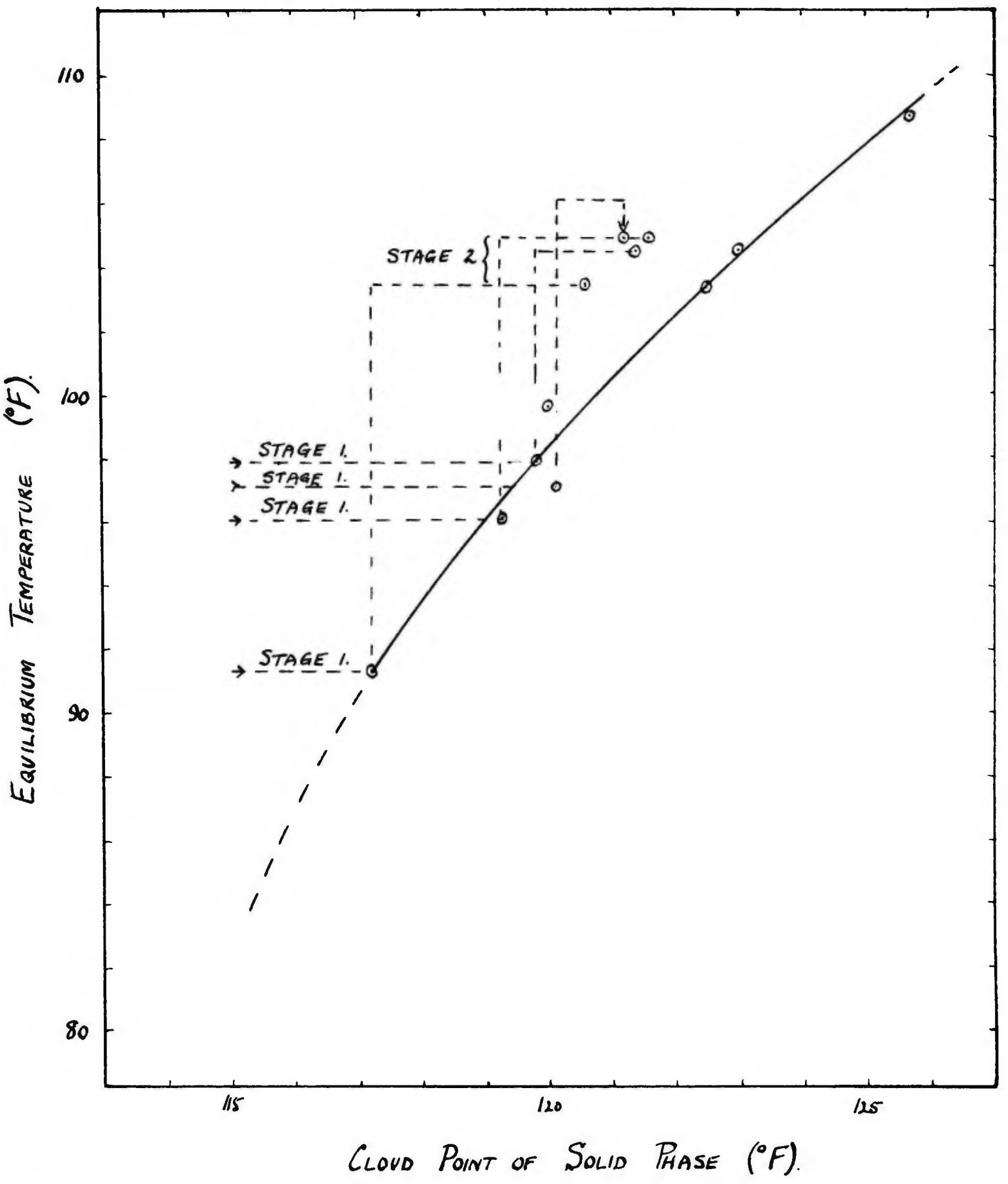

110
100
90
80
STAGE 2
STAGE 1.
STAGE 1.
STAGE 1.
STAGE 1.
115
120
125
EQUILIBRIUM TEMPERATURE (°F).
CLOUD POINT OF SOLID PHASE (°F).

FIG. 12.

results in a higher yield of lower cloud-point solid than that obtained in a one-stage removal at the higher of the two equilibrium temperatures.

The results of the last four experiments are illustrated in Fig. 12 opposite, from which it seems that an equilibrium diagram similar to that shown in Fig. 11 applies only to a one-stage removal of liquid phase, and is not applicable to the multi-stage (or more correctly - infinite-stage) removal of liquid phase which constitutes the ideal process for the separation of paraffin waxes by fractional melting.

With the object of securing further information concerning the nature of the equilibrium diagram representing the ideal process, it was decided to perform a series of similar experiments on various mixtures of two commercial paraffin waxes.

(C) Blends of Two Commercial Waxes

Two refined commercial waxes (1) Burma 108°F. melting (L.M.) of cloud-point 108.3°F. and (2) a "135/140°F. melting" wax (H.M.) of cloud-point 135.5°F. were blended in the proportions given below to form waxes of the cloud-points shown :-

(a) 30% H.M. + 70% L.M. Resultant wax of cloud-point 116.7°F.
(b) 50% H.M. + 50% L.M. " " " " 122.8°F.
(c) 75% H.M. + 25% L.M. " " " " 129.3°F.

The equilibrium diagram was obtained for each of these blends in exactly the same manner as for the Anglo-Iranian Slack Wax and the de-oiled Slack Wax. Experimental data are given in Table VII (Page 46).

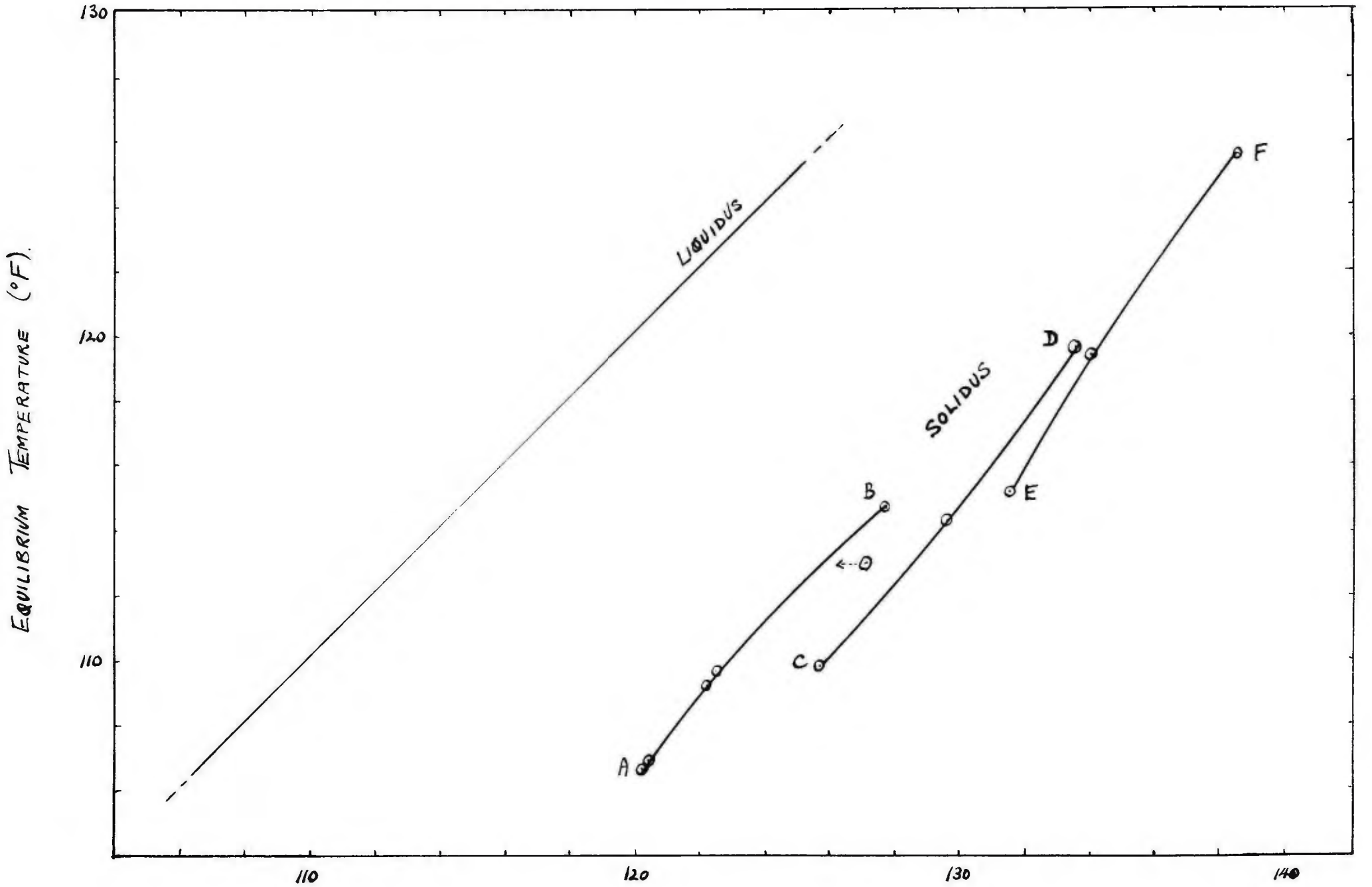

130
120
110
EQUILIBRIUM TEMPERATURE (°F).
LIQUIDUS
SOLIDUS
A
B
C
D
E
F
110
120
130
140
CLOUD POINT (°F).

FIG. 13.

TABLE VII.

Wax Blend	Expt.	Equil. Temp.	% by Weight		Cloud-Point	
			Solid Phase	Liquid Phase	Solid Phase	Liquid Phase
(a) 30% H.M./ 70% L.M.	1.	106.7	74.1	25.9	120.1	106.6
Cloud Point 116.7°F.	2.	109.2	54.8	45.2	122.3	109.0
	3.	109.2	56.1	43.9	122.1	109.2
	4.	113.2	26.9	73.1	127.1	113.0
	5.	115.0	17.5	82.5	127.7	114.7
(b) 50% H.M./ 50% L.M.	6.	110.0	82.9	17.1	125.6	109.8
Cloud Point 122.8°F.	7.	114.5	52.9	47.1	129.6	114.3
	8.	120.0	19.9	80.1	133.5	119.7
(c) 75% H.M./ 25% L.M.	9.	115.4	86.9	13.1	131.6	115.2
Cloud Point 129.3°F.	10.	119.5	68.2	31.8	134.0	119.5
	11.	126.0	29.9	70.1	138.5	125.7

The above data are represented graphically in Fig. 13 opposite, where AB, CD, and EF represent the solidus curves for the wax blends of cloud-points 116.7°, 122.8°, and 129.3°F. respectively.

Assuming cloud-point to be an additive property for the blends of commercial waxes, the yield of solid phase was calculated, as shown previously, for each of the experiments given in the above Table. Agreement between experimental and calculated

values is fair, as shown in Table VIII below :-

TABLE VIII.

Expt.	Equilibrium Temperature	% Yield - Solid Phase		
		Experimental	Calculated	Experimental - Calculated
1.	106.7	74.1	74.8	- 0.7%
2.	109.2	54.8	57.9	- 3.1%
3.	109.2	56.1	58.1	- 2.0%
4.	113.2	26.9	26.2	+ 0.7%
5.	115.0	17.5	15.4	+ 2.1%
6.	110.0	82.9	82.3	+ 0.6%
7.	114.5	52.9	55.5	- 2.6%
8.	120.0	19.9	22.4	- 2.5%
9.	115.4	86.9	86.0	+ 0.9%
10.	119.5	68.2	67.6	+ 0.6%
11.	126.0	29.9	28.1	+ 1.8%

It was considered possible that the equilibrium curve for the solid phase of cloud-point 122.8°F. obtained from the wax blend of cloud-point 116.7°F. might follow the equilibrium curve for the blend of cloud-point 122.8°F., and thus the curve CD (Fig. 13) would be applicable to this solid phase. Similarly, the equilibrium curves for the two solid phases of cloud-point 129.3°F. obtained from the blends of cloud-point 116.7°F. and

122.8°F. respectively by removal of the liquid phase at the appropriate equilibrium temperatures, might fall along EF (Fig. 13), the equilibrium curve for the blend of cloud-point 129.3°F.

This, however, did not prove to be the case, as is shown by the following results.

The cloud-point, 122.3°F., of the solid phase in Experiments 2 and 3 (Table VII) is not appreciably different from that of the 50/50 blend, to which the equilibrium curve CD (Fig. 13) is applicable. This solid phase was therefore allowed to reach equilibrium at a temperature of 113.0°F. and the usual procedure followed for the separation of the liquid and solid phases. This experiment resulted as follows :-

Solid Phase: Cloud-Point 125.3°F. Yield 77.5%

Liquid Phase: Cloud-Point 112.8°F. Yield 22.5%

It is clear, from reference to Fig. 13., that this two-stage removal of liquid phase results in a solid phase of slightly lower cloud-point than that obtained in a one-stage removal at the higher equilibrium temperature.

The above results were confirmed by a second series of experiments which gave the following figures :-

	Equil. Temp.	% by Weight Solid Phase	% by Weight Liquid Phase	Cloud Point Solid Phase	Cloud-Point Liquid Phase
(1st Stage	107.0	69.6	30.3	120.3	106.9
(2nd Stage	113.9	49.0	51.0	126.9	113.8
1st Stage	113.8	22.6	77.4	127.3	113.5

Yield Summary for twe-stage Experiment :-

30.3% Liquid Phase of Cloud-Point 106.9°F.

35.7% Liquid Phase of Cloud-Point 113.8°F.

34.1% Solid Phase of Cloud-Point 126.9°F.

The experiments with the blends of low and higher melting commercial waxes confirm the chief finding with the de-oiled Anglo-Iranian Slack Wax, as a two-stage removal of the liquid phase results in a higher yield of lower melting solid phase than is obtained in a one-stage removal of the liquid phase at the higher equilibrium temperature. An additional finding of importance, however, emerges from these experiments. Two different mixtures of waxes having the same cloud-point but differing in composition will not give similar solidus/liquidus equilibrium diagrams, and it becomes clear, therefore, that the equilibrium diagram ultimately obtained, which represents the process of fractional melting of any particular wax stock, will apply only to the stock for which

it is determined, and it will not apply to other stocks having the same cloud-point.

The practical application of any equilibrium diagram obtained is thus restricted, as the diagram would have to be determined for each wax stock, and it is now obvious that this is likely to prove a difficult and tedious operation. However, the construction of the diagram is of considerable academic interest and a more detailed knowledge of its nature is therefore of importance.

Summary of Essential Deductions from Preliminary Work.

At this stage a brief résumé may be given of the progress of the investigation, indicating the extent to which essential information leading to a satisfactory solution of the problem, has been furnished. The work, as previously explained, has as its object the application of phase rule principles to a study of the separation of paraffin waxes of different melting points by the process of fractional melting, with the ultimate intention of applying the equilibrium curve obtained, to a study of the sweating process used in the commercial production of paraffin wax.

The first essential is the construction of the equilibrium diagram and the experiments already described - although rather numerous owing to the complex nature of wax - must be considered as being of an exploratory character only, inasmuch as they furnish a limited amount of information concerning the nature of the diagram, whilst at the same time giving an indication of its limitations, which have been mentioned above. The following may be considered the pertinent observations :-

(1) Using slack-wax, difficulties are introduced which cannot be readily surmounted and it is therefore advisable to work with an oil-free wax mixture (P. 37).

It is now clear that the determination of the equilibrium diagram must be followed by experiments on the fractional

melting of the wax stock under varying conditions. The process of sweating may then be examined by making a comparative study of the results obtained with various synthetic mixtures comprising the wax stock used in the determination of the equilibrium diagram and a particular wax-free oil (or oils).

(2) The equilibrium diagram for an oil-free wax blend is somewhat different from that given by naphthalene and β-naphthol - a typical example of the type of diagram given by two substances forming a continuous series of solid solutions. It is expected, however, that the two diagrams will be comparable in certain respects, and that any discrepancies might be attributed to the melting range of the wax.

(3) The equilibrium diagram applicable to the process of fractional melting of waxes cannot be obtained by the one-stage separation of solid and liquid phases at different equilibrium temperatures covering the melting range of the wax. It is clear that as the ideal process of separation consists in completely removing the liquid phase at each infinitesimally small temperature increment, an approach to the equilibrium diagram representing this ideal process may be obtained by actually removing the liquid phase in as many stages as is conveniently and experimentally practicable, and subjecting the solid and liquid phases to the necessary tests at each stage.

(4) The apparatus used in the equilibrium experiments so far described is not entirely satisfactory and an improvement can be made in the method of separating the two wax phases.

(5) The possibility of using some property other than cloud-point to characterise the phases must be investigated, as cloud-point, besides not being additive, is also a property not used commercially in connection with waxes.

Consideration is given to this problem in the pages immediately following.

Physical Property for Characterisation of Wax Phases.

The essentials of the physical property to be used for the characterisation of the phases are as follows :-

(1) It must be "additive" in order that the equilibrium diagram shall apply quantitatively as well as qualitatively, i.e. it must be such that if equal amounts of two different waxes are taken, then the property of the blend must be the mean of those of the two waxes.

(2) It should be capable of accurate determination, as the melting range of the wax stock is limited (the wax stock used in the later work contains constituents melting within the range 105 - 142°F.).

(3) It should preferably be related to the melting point as this is, from the industrial viewpoint, the most important property of a wax.

As wax consists of more than two compounds, any physical property will be merely an average property and will not, in general, give an indication of the composition of the wax. If, for example, three normal paraffins P_1, P_2, P_3, have molecular weights (in increasing order) of M_1, M_2, and M_3 respectively, then there is an infinitely large number of blends of P_1, P_2 and P_3 each having a molecular weight of M, where M is intermediate between M_1 and M_3.

The physical properties, other than cloud-point, which might possibly be used are as follows :-

(a) molecular weight

(b) refractive index

(c) specific gravity

(d) aniline point

and (e) melting point.

These properties will now be discussed in greater detail.

(a) Molecular Weight

Molecular weight is, of course, an additive property, and the only argument against its use is the difficulty of determination in the case of waxes. Using even the ebullioscopic apparatus of Menzies[64], and extrapolating the molecular weight values to infinite dilution, it is difficult to guarantee an accuracy of 2%.

Considering this limit of accuracy with reference to n-docosane and n-octacosane - two n-paraffins whose melting points are within the wax range -

n-docosane	M.W.	310.4	M.Pt.	112.1°F.
n-octacosane	M.W.	394.4	M.Pt.	142.9°F.

it is observed from these values that, for an increase of 394.4 - 310.4 = 84 in molecular weight, the melting point is raised by 142.9 - 112.1 = 30.8°F. Thus, the melting point is affected to the extent of 0.3°F. for each unit increase in

molecular weight.

Assuming even that the molecular weight may be estimated with an accuracy of 1% - a figure never attained in practice - the experimental error on a molecular weight of 300 would be 3 units, equivalent to 3 x 0.3 = 0.9°F. With a probable error of such magnitude in the determination, molecular weight is therefore an unsuitable property for use in the construction of the equilibrium diagram where accuracy to within 0.1°F. is essential.

The assumption that the increase in molecular weight affects the melting point of waxes to approximately the same extent as the two n-paraffins considered, is justified, for although the molecular weight/melting point curve for normal commercial waxes is, in general, slightly displaced from the corresponding curve for n-paraffins of molecular weight within the wax range, it is nearly parallel to the latter.

(b) Refractive Index

Refractive index is a property which may be determined rapidly and with accuracy and, moreover, only a very small quantity of material is needed for the determination. For waxes of melting point lower than 60°C. the refractive index of the liquid sample is usually determined at 60°C. For the present work, an Abbé Refractometer was available with which it was possible to estimate the refractive index to 0.0001.

The following are typical values for the refractive indices measured at 60°C. (n_D^{60}). of fractions collected in Laboratory sweatings of the wax stock employed in the later stages of this work :-

TABLE IX.

M.Pt.	n_D^{60}
112.6	1.4328
119.4	1.4334
127.05	1.4345
137.3	1.4362
142.7	1.4373

These figures indicate that the value of n_D^{60} increases by approximately 0.00015 for each 1°F. increase in melting point, and as n_D^{60} can be estimated to 0.0001, the possible error is more than 0.6°F. The property of refractive index cannot, therefore, be used.

(c) Specific Gravity.

Figures given in the literature for melting point versus specific gravity of wax are very variable, but the following data given by Morris and Adkins[65] for American wax may be cited to give an indication of the relation between the two properties :-

Melting Point	$d^{130^{\circ}F.}_{60^{\circ}F.}$
103	0.778
109	0.777
115	0.780
118	0.782

It is clear that the specific gravity varies only slightly with melting point, and even assuming that the values for the waxes of 115° and 118°F. melting point are typical, it is observed that a difference of 3°F. affects the specific gravity by only 0.002. The specific gravity of a wax is not normally required to more than 0.001, and as it is very doubtful whether the value may be conveniently determined to an accuracy of 0.0002, this property is not sufficiently accurate.

(d) Aniline Point.

The aniline point of wax may be readily determined, and with care, individual readings do not normally differ by more than 0.2°C. A linear relationship exists between melting point and aniline point which can be expressed by the equation:- [70.]

$$\text{Aniline Point (in } ^{\circ}C.) = 0.319 \times \text{Melting Point (in } ^{\circ}F.) + 75.6$$

Thus, an increase of 0.319°C. in aniline point represents an increase of 1°F. in melting point. Assuming that the aniline point could be determined to 0.1°C, the possible experimental error would then be equivalent to 0.3°F. in melting point.

Aniline point is therefore the most promising of the properties reviewed, and is likely to lead to more accurate results than any other of the properties. The linear relationship between aniline point and melting point is, however, of special significance, as this means that if melting point is non-additive then aniline point also is non-additive. Now it will be shown later that a modification of the I.P.T. Setting Point method (Serial Designation P.S.11a.) may be used to determine melting point with an accuracy of 0.05°F., and it is clear therefore that no advantage is to be gained by using the property of aniline point in preference to melting point, especially as the latter is quite as easy to determine.

(e) Melting Point.

Contrary to the statement of Gault and Boisselet,[61] it was found that the melting point of a mixture of waxes could not be calculated from the rule of mixtures, and melting point is therefore not strictly an additive property. Blends of various waxes were found to have melting points slightly higher than the values calculated from the rule of mixtures. This was confirmed by the determination of the melting points (using the I.P.T. Setting Point Method) for blends of two Anglo-Iranian commercial waxes of melting points 130.95°F.(H) and 108.35°F.(L) respectively, over the complete range 100%H to

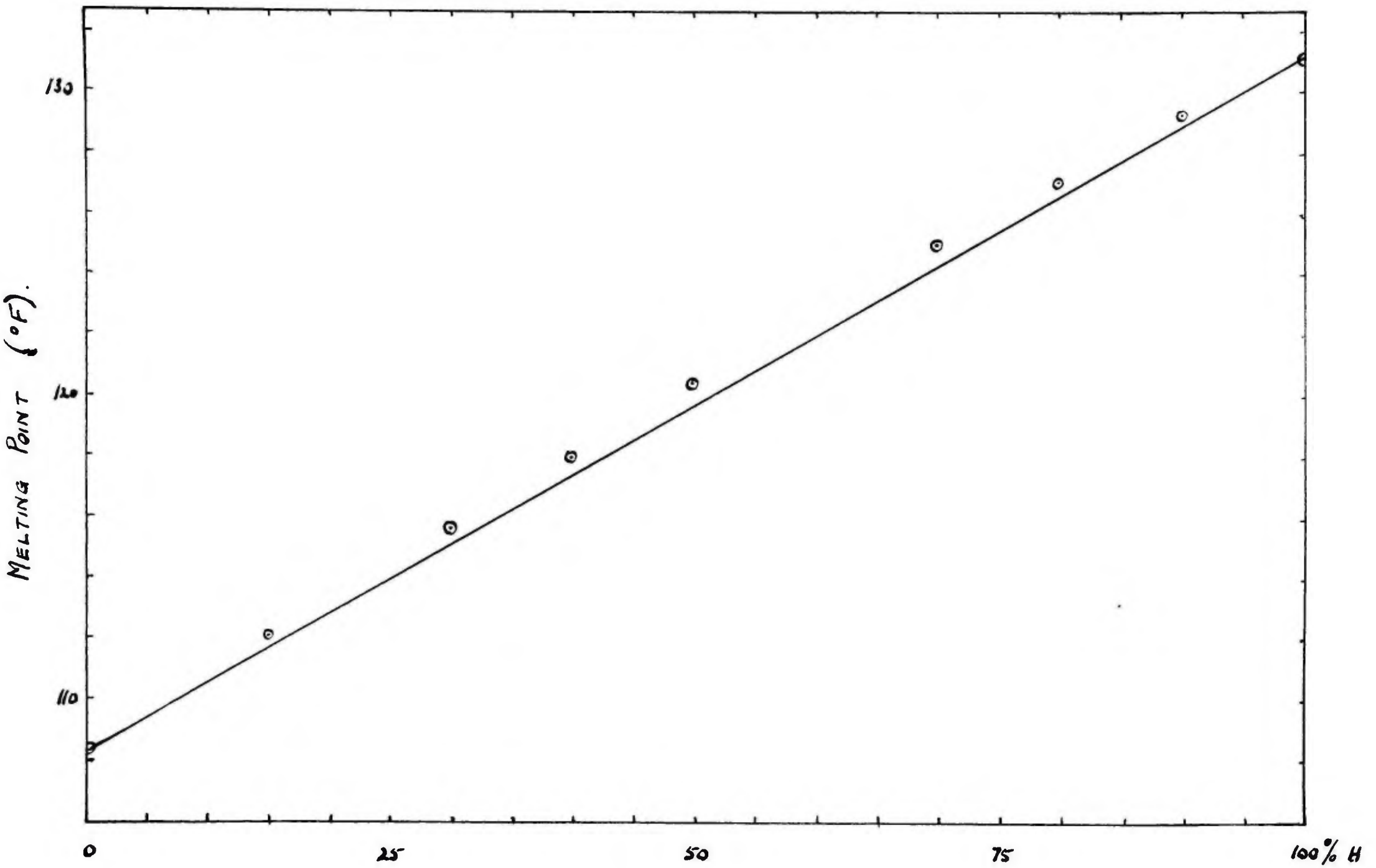

MELTING POINT (°F).
130
120
110
0
25
50
75
100% H
PER CENT HIGH M. Pt. WAX IN BLEND.

FIG. 14.

100%L. Figures are given in Table X. below and are represented graphically in Fig. 14 opposite.

TABLE X.

% H.	100	90	80	70	50	40	30	14.9	0
% L.	0	10	20	30	50	60	70	85.1	100
Mt.Pt.	130.95	129.15	126.95	124.9	120.4	118.0	115.65	112.1	108.35

It is clear from Fig. 14 that the experimental values do not lie on the straight line joining the melting points of H and L.

The non-additivity of melting point is further illustrated by the following results given by Berne-Allen[66] and Work for certain wax blends. The values calculated by the law of mixtures are included.

TABLE XI.

Blend	M.Pt. (Berne--Allen)	M.Pt. Calculated
Equal wts. of 52.8°C. and 64.4°C. M.Pt. waxes	59.1°C.	58.6°C.
Equal wts. of waxes of following M.Pts.:- 49.9, 52.8, 55.6, 60.3 and 64.4°C.	56.9°C.	56.6°C.

It will be noted that the experimental is slightly higher than the calculated value.

As would be expected, it is found that the smaller the difference between the melting points of the two stock waxes, the smaller is the deviation from the straight line (Fig. 14). For example, a 50/50 blend of two Anglo-Iranian waxes of melting points 130.95° and 119.85°F. respectively, was found to have a

melting point of 125.6°F., compared with the calculated figure of 125.4°F.

It is to be concluded that there is no physical property of wax entirely satisfactory for use in the construction of the equilibrium diagram, but of all the possible properties, that of melting point is undoubtedly the most suitable as

(a) it may be determined without difficulty to within 0.05°F. using a simple apparatus, and

(b) although not strictly additive, there is not a great difference between the experimental values and those calculated on the assumption that it is additive.

There is a further justification for its use, for although commercially refined paraffin wax must meet definite minimum oil content and colour requirements, it is marketed primarily on the basis of melting point specifications, and in a research of this nature it is essential that the industrial application should be kept in mind.

It was therefore decided to use melting point for the characterisation of waxes.

Melting Point of Wax as a Function of Molecular Weight.

Now molecular weight is strictly additive and although, as already stated, its direct use is not possible in this work owing to the comparatively large experimental errors involved in its determination, it was considered advisable to investigate the possibility of its indirect use.

It was noticed that the melting point/composition curve for mixtures of two waxes (Fig. 14. Page 60a) was similar in form to the melting point/molecular weight curve for the n-paraffins within the wax range (see Fig. 16. Page 67a - molecular weight range 200 - 300). The obvious course was to proceed on the assumption that the wax consisted of a mixture of n-paraffins, and the melting point/molecular weight curve for these hydrocarbons was therefore drawn from the most reliable figures to be found in the literature. From this curve was found the molecular weight of the hypothetical n-paraffin corresponding to the melting point of any particular wax, and this value was assumed to be the molecular weight of the wax. The yields of the solid and liquid phases obtained in the equilibrium experiments (Page 83) were then calculated using this assumed molecular weight as the additive property, and it was found that the agreement between experimental and calculated figures was, in general, closer than when melting point alone was used as the additive property. The investigation was developed and an equation was deduced showing the relationship between melting point and molecular

weight in the n-paraffin series.[67] This interesting and fundamental relationship has been applied with considerable success in later sections of this work and an account is therefore given of its derivation. Such a study necessarily includes a consideration of the n-paraffins of lower molecular weight and this, although of importance (it is suggested that further study along these lines might ultimately be of value in elucidating the structure of the first members of the series), is somewhat outside the scope of the main research, but is nevertheless included for the purposes of continuity and completeness.

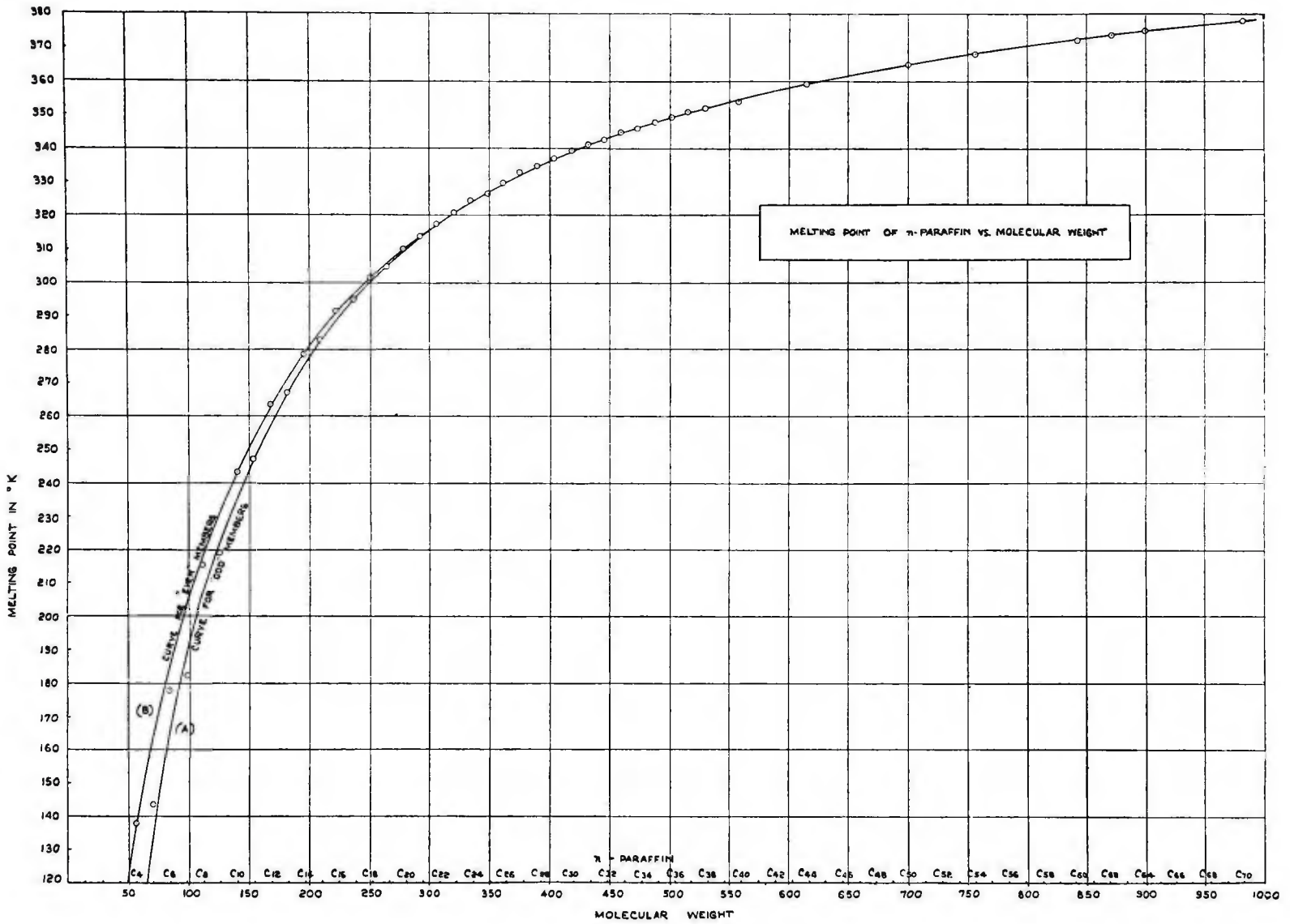

MELTING POINT OF n-PARAFFIN VS. MOLECULAR WEIGHT
MELTING POINT IN °K
MOLECULAR WEIGHT
n - PARAFFIN
CURVE FOR EVEN NUMBERS
CURVE FOR ODD NUMBERS
(A)
(B)

FIG. 15.

Relation between Melting Point and Molecular Weight in the n-Paraffin series.

In Fig. 15, curves A and B show, for the odd and even members, respectively, the melting point of the n-paraffin plotted against its molecular weight. Considerable choice in melting point is afforded by the literature for many members of the series, but the values used have been selected after careful consideration and, in the opinion of the *authors[67], represent the most reliable figures.

It is evident from Fig. 15 that the odd and even members of the series lie on different curves, and it is therefore obvious that no one equation connecting melting point and molecular weight will suffice to represent to any degree of accuracy both the odd and even members over the whole series of n-paraffins. It is seen, however, that with increase in the number of carbon atoms in the molecule, the curves tend to converge, and the difference between them from C_{22} onwards is so small that they may be considered as being coincident - i.e. a smooth curve may be drawn through the plots.

An expression connecting the melting point with the corresponding molecular weight which is applicable especially to this smooth curve may be obtained in the following manner :-

* Etessam and Sawyer.

Let M = molecular weight of an n-paraffin of melting point = T°K.

Assume $\frac{dM}{dT} = k\phi^2$, where $\phi = f(M) = aM + b$

where k, a and b are constants.

Then $\frac{dM}{dT} = k(aM + b)^2$

$$\therefore \quad dT = \frac{1}{k} \frac{dM}{(aM + b)^2}$$

$$\therefore \int dT = \frac{1}{k} \cdot \int \frac{dM}{(aM + b)^2}$$

i.e., $$T = -\frac{1}{ak} \cdot \frac{1}{(aM + b)} + \text{const.} \quad \ldots\ldots\ldots (1)$$

When $T = 0$, $M = 0$, $\therefore$ const. $= \frac{1}{akb}$

Equation (1) now becomes

$$T = \frac{1}{akb} - \frac{1}{ak} \cdot \frac{1}{(aM + b)}$$

$$= \frac{1}{akb} \left\{ 1 - \frac{1}{\frac{aM}{b} + 1} \right\}$$

$$= \frac{1}{akb} \cdot \frac{\frac{a}{b}M}{\frac{aM}{b} + 1}$$

$$= \frac{1}{akb} \cdot \frac{1}{1 + \frac{b}{aM}}$$

i.e. $$T = T_f \cdot \frac{1}{(1 + \frac{c}{M})} \quad \ldots\ldots\ldots\ldots\ldots (2)$$

where T_f and c are both constant, being equal to $\frac{1}{akb}$ and $\frac{b}{a}$, respectively.

Equation (2) may be expressed in the form :-

$$T_f = T\left(1 \neq \frac{c}{M}\right) = T_{(x)}\left(1 \neq \frac{c}{M_{(x)}}\right) = T_{(y)}\left(1 \neq \frac{c}{M_{(y)}}\right)$$

from which $$c = \frac{T_{(y)} - T_{(x)}}{\frac{T_{(x)}}{M_{(x)}} - \frac{T_{(y)}}{M_{(y)}}}$$

The constant c may therefore be calculated from a knowledge of the melting points and molecular weights of any two n-paraffins. The average figure of c = 94.4 was obtained from a number of such calculations. By substituting this value of c in equation (2), T_f (which obviously represents the convergence temperature) is found to be 414.5°K.

Equation (1) connecting the melting point (T°K.) and molecular weight (M) of the n-paraffin then becomes :-

$$T = \frac{414.5}{\left(1 \neq \frac{94.4}{M}\right)} \quad \text{or} \quad \frac{414.5M}{(M \neq 94.4)} \quad \ldots\ldots\ldots (3)$$

* THE "≠" SIGN SHOULD BE READ AS "+".

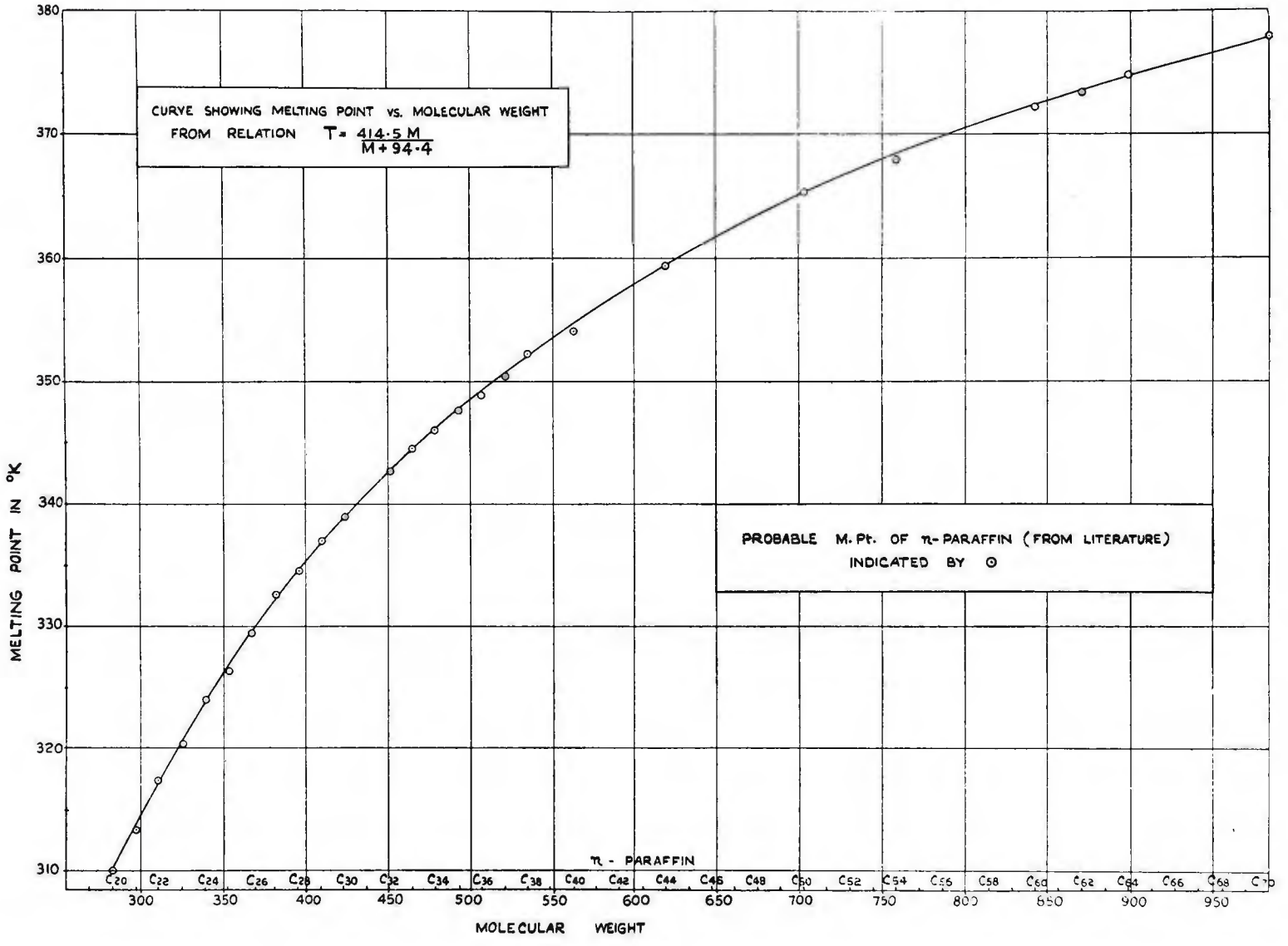

CURVE SHOWING MELTING POINT vs. MOLECULAR WEIGHT
FROM RELATION T = 414·5 M / M + 94·4
PROBABLE M. Pt. OF n-PARAFFIN (FROM LITERATURE)
INDICATED BY ⊙
MELTING POINT IN °K
380
370
360
350
340
330
320
310
n - PARAFFIN
C20 C22 C24 C26 C28 C30 C32 C34 C36 C38 C40 C42 C44 C46 C48 C50 C52 C54 C56 C58 C60 C62 C64 C66 C68 C70
300 350 400 450 500 550 600 650 700 750 800 850 900 950
MOLECULAR WEIGHT

FIG. 16

In Table 12 below are tabulated for the known n-paraffins, between C_{22} and C_{70} (a) the molecular weight, (b) the most reliable value of the melting point given in the literature, (c) the value of the melting point calculated from equation (3), and (d) the difference between the experimental and calculated figures.

TABLE XII.

Member of Series.	Molecular Weight.	Melting Point, ° K. (from Literature).	Melting Point, ° K. (from relation $T = \frac{414{\cdot}5M}{94{\cdot}4 + M}$).	Experimental — Calculated Melting Point.
C_{22}	310·4	317·5	317·9	−0·4
C_{23}	324·4	320·4	321·0	−0·6
C_{24}	338·4	324·1	324·1	±0·0
C_{25}	352·4	326·3	326·9	−0·6
C_{26}	366·4	329·6	329·6	±0·0
C_{27}	380·4	332·5	332·1	+0·4
C_{28}	394·4	334·6	334·5	+0·1
C_{29}	408·5	336·9	336·7	+0·2
C_{30}	422·5	339·0	338·8	+0·2
C_{31}	436·5	340·8	340·8	±0·0
C_{32}	450·5	342·6	342·7	−0·1
C_{33}	464·5	344·5	344·5	±0·0
C_{34}	478·5	345·8	346·2	−0·4
C_{35}	492·6	347·6	347·9	−0·3
C_{36}	506·6	348·8	349·3	−0·5
C_{37}	520·6	350·4	350·9	−0·5
C_{38}	534·6	352·2	352·3	−0·1
C_{39}	548·6	—	353·6	—
C_{40}	562·6	353·75 (±0·25)	354·9	−0·9
C_{44}	619·7	359·4	359·6	−0·2
C_{50}	702·8	365·1 (±0·2)	365·3	±0·0
C_{54}	758·9	368·0	368·7	−0·7
C_{60}	842·9	371·9 (±0·4)	372·8	−0·5
C_{62}	871·0	373·5	374·0	−0·5
C_{64}	899·0	375	375·1	−0·1
C_{70}	983·1	378·25 (±0·25)	378·2	±0·0

A graphical representation of Table 12 is given in Fig. 16.

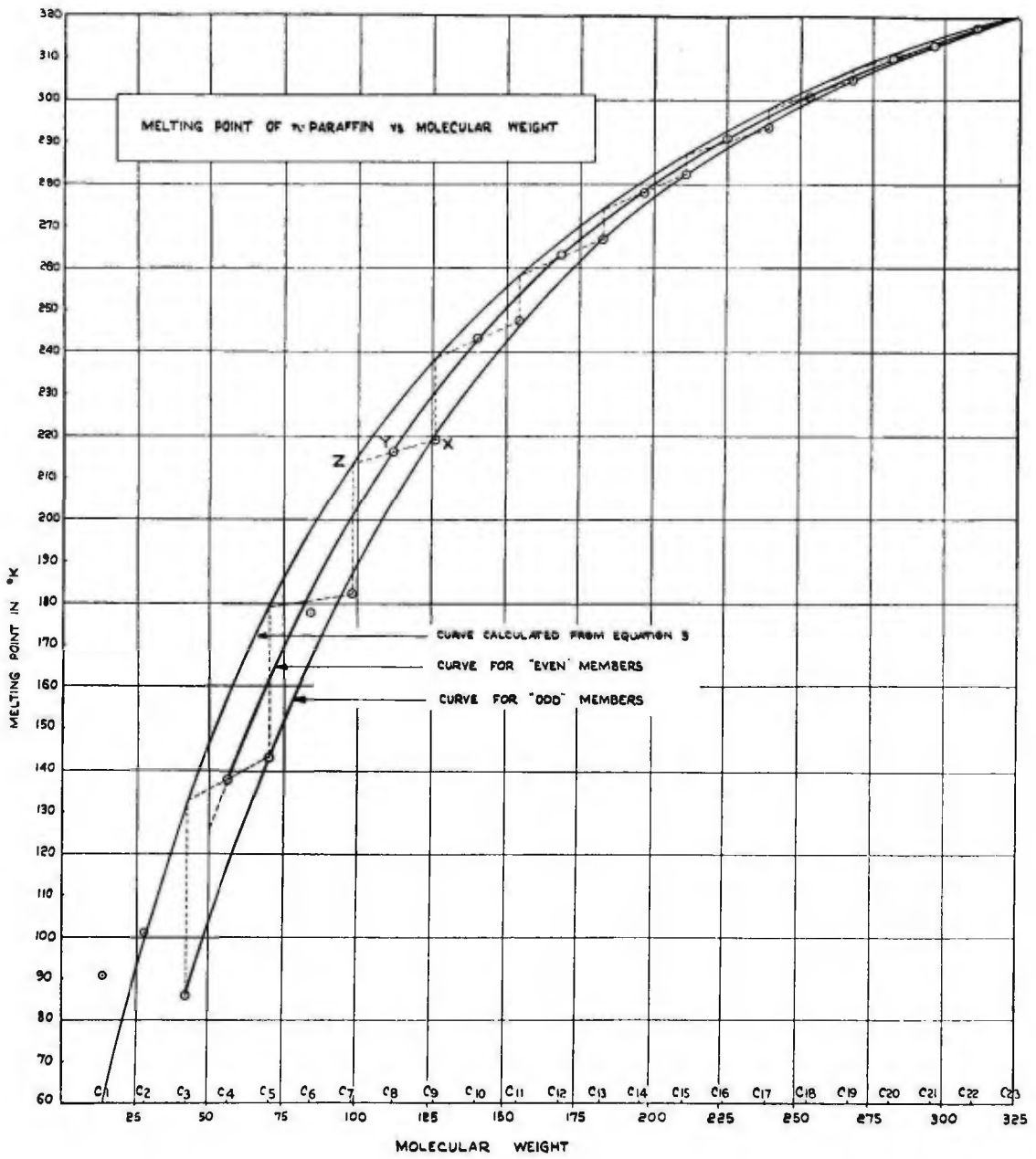

MELTING POINT OF n-PARAFFIN vs MOLECULAR WEIGHT
MELTING POINT IN °K
MOLECULAR WEIGHT
CURVE CALCULATED FROM EQUATION 3
CURVE FOR "EVEN" MEMBERS
CURVE FOR "ODD" MEMBERS
X
Y
Z
320
310
300
290
280
270
260
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
C1 C2 C3 C4 C5 C6 C7 C8 C9 C10 C11 C12 C13 C14 C15 C16 C17 C18 C19 C20 C21 C22 C23
25 50 75 100 125 150 175 200 225 250 275 300 325

FIG. 17.

The difference between the experimental and calculated figures is within 1°C. for all known members of the series having more than twenty-one carbon atoms in the molecule, and equation (3) may therefore be considered to represent the relation between melting point and molecular weight for the n-paraffins having molecular weight greater than 300.

With the lower members of the series, the difference between the actual values and those calculated from equation (3) in general increases with decrease in the number of carbon atoms in the molecule, the difference being greater for the odd than for the even members, a fact well illustrated in Fig. 17, which shows the molecular weight and melting-point curve for this lower region drawn on a larger scale. Although the formula is not applicable with any degree of accuracy when the number of carbon atoms in the molecule is less than twenty-two, nevertheless there exists between the three curves shown in Fig. 17, a very interesting relation, which is of particular importance in its application to these lower members.

Consider, for example, the three n-paraffins C_7H_{16}, C_8H_{18} and C_9H_{20} (Fig. 17). Let X on the "odd" curve represent the actual melting point of C_9H_{20}, and let Z= melting point of C_7H_{16} on the curve calculated from equation (3). Join XZ and bisect at Y. It is found that the point Y coincides with the actual melting point of C_8H_{18} given on the "even" curve.

Thus, if $T_{(9)}$ = actual melting point of C_9H_{20} ("odd curve")

$T_{(8)}$ = " " " " C_8H_{18} ("even curve")

and $\dfrac{414.5}{1 + \frac{94.4}{M_{(7)}}}$ = melting point of C_7H_{16} calculated from equation (3)

then $$T_{(8)} = \tfrac{1}{2}\left\{\left(T_{(9)} + \frac{414.5}{1 + \frac{94.4}{M_{(7)}}}\right)\right\} \quad \ldots\ldots\ldots\ldots (4)$$

This relation (with two exceptions only) is found to be true in each case. For those members containing more than twenty-one carbon atoms the "calculated" curve is removed only slightly from the actual, and the relation is applicable to this region because the melting points of successive members increase by small and fairly regular increments.

Generally, if the number of carbon atoms in the molecule is given by (n - 1), (n), (n + 1), where n is an even integer, then the melting point $T_{(n)}$ of the "even" compound is given by the expression

$$T_{(n)} = \tfrac{1}{2}\left\{\left(T_{(n+1)} + \frac{414.5}{1 + \frac{94.4}{M_{(n-1)}}}\right)\right\} \quad \ldots\ldots\ldots (5)$$

where $T_{(n+1)}$ = actual melting point of $C_{(n+1)}$ n-paraffin, and $M_{(n-1)}$ = molecular weight of $C_{(n-1)}$ n-paraffin.

Using the most reliable figures given in the literature for the melting point of the "odd" n-paraffins (Tabulated in Table 12, column 3), the melting points of the "even" members have been calculated from equation (5). With two exceptions only (C_2 and C_6), the agreement between experimental and calculated values is within 1°C., as shown in Table 13.

TABLE XIII.

Member of Series.	Molecular Weight.	Melting Point, ° K. (from Literature).	Melting Point, ° K. (calculated from Equation 5).	Experimental — Calculated Melting Point.
C_2	30·0	101	73·0	+28·0
C_4	58·1	138·0	137·6	+ 0·4
C_6	86·1	177·6	180·9	− 3·3
C_8	114·1	216·2	216·4	− 0·2
C_{10}	142·2	243·3	242·1	+ 0·2
C_{12}	170·2	263·4	260·9	+ 0·5
C_{14}	198·2	278·5	278·6	− 0·1
C_{16}	226·3	291·1	291·0	+ 0·1
C_{18}	254·3	301·0	301·3	− 0·2
C_{20}	282·3	310·0	310·1	− 0·1
C_{22}	310·4	317·5	317·4	+ 0·1
C_{24}	338·4	324·1	323·7	+ 0·4
C_{26}	366·4	329·6	329·7	− 0·1
C_{28}	394·4	334·6	334·5	+ 0·1
C_{30}	422·5	339·0	338·8	+ 0·2
C_{32}	450·5	342·6	342·7	− 0·1
C_{34}	478·5	345·8	346·1	− 0·3
C_{36}	506·6	348·8	349·2	− 0·4

Equation 5 may be expressed in the form

$$T_{(n\neq1)} = 2T_{(n)} - \frac{414.5}{1 \neq \frac{94.4}{M_{(n-1)}}}$$

and obviously gives $T_{(n\neq1)}$, where $T_{(n)}$ is known - i.e. the melting point of an "odd" member may be calculated from a knowledge of the melting point of the preceding "even" member

and the molecular weight of the preceding "odd" member. With two exceptions only (C_3 and C_7) the agreement between experimental and calculated values is within 1°C., as shown in Table 14 below :-

TABLE XIV

Member of Series.	Molecular Weight.	Melting Point, ° K. (from Literature).	Melting Point, ° K. (calculated from Equation 5).	Experimental — Calculated Melting Point.
C_1	16·0	90·4	—	—
C_3	44·1	85·9	141·8	−55·9
C_5	72·1	143·3	144·1	− 0·8
C_7	100·1	182·4	175·8	+ 6·6
C_9	128·2	219·3	219·0	+ 0·3
C_{11}	156·2	247·4	247·9	− 0·5
C_{13}	184·2	267·5	268·5	− 1·0
C_{15}	212·2	283·0	283·9	− 0·9
C_{17}	240·3	295·0	295·3	− 0·3
C_{19}	268·3	305·0	304·4	+ 0·6
C_{21}	296·3	313·4	313·1	+ 0·3
C_{23}	324·4	320·4	320·6	− 0·2
C_{25}	352·4	326·3	327·2	− 0·9
C_{27}	380·4	332·5	332·1	+ 0·4
C_{29}	408·4	336·9	337·1	− 0·2
C_{31}	436·5	340·8	341·3	− 0·5
C_{33}	464·5	344·5	344·4	+ 0·1
C_{35}	492·6	347·6	347·1	+ 0·5
C_{37}	520·6	350·4	349·7	+ 0·7

SUMMARY.

1. The melting point of any normal paraffin having more than twenty-one carbon atoms in the molecule may be calculated from the relation :-

$$T = \frac{414.5M}{M + 94.4}$$

where T = melting point in °K. of the n-paraffin of molecular weight = M.

2. From the relation :-

$$T_{(n)} = \tfrac{1}{2}\left(T_{(n\neq1)} + \frac{414.5M_{(n-1)}}{M_{(n-1)} + 94.4}\right)$$

where n = even integer

$T_{(n)}$ = melting point in °K. of C_n n-paraffin

$T_{(n\neq1)}$ = melting point in °K. of $C_{n\neq1}$ "

$M_{(n-1)}$ = molecular weight of C_{n-1} "

the melting point of C_n may be calculated when the melting point of $C_{n\neq1}$ is known, and vice versa.

With four exceptions only (C_2, C_3, C_6, C_7) the agreement between experimental and calculated values is within 1°C., and in this connection it will be noted from Fig. 17 that the reported values for C_6 and C_7 do not lie on the respective curves, and that the melting point of C_3 is abnormal, as it is lower than the melting points of C_1 and C_2.

The equation $T = \frac{414.5M}{94.4+M}$ is applied in the following manner to the calculation of melting points of wax blends. The actual melting points T_1, T_2.... of the constituent waxes are substituted for T in the equation and the hypothetical molecular weights M_1, M_2.... thus obtained. The hypothetical molecular weight of the blend is then calculated by the rule of mixtures and the value substituted in the equation, thus giving T, for the calculated melting point of the blend.

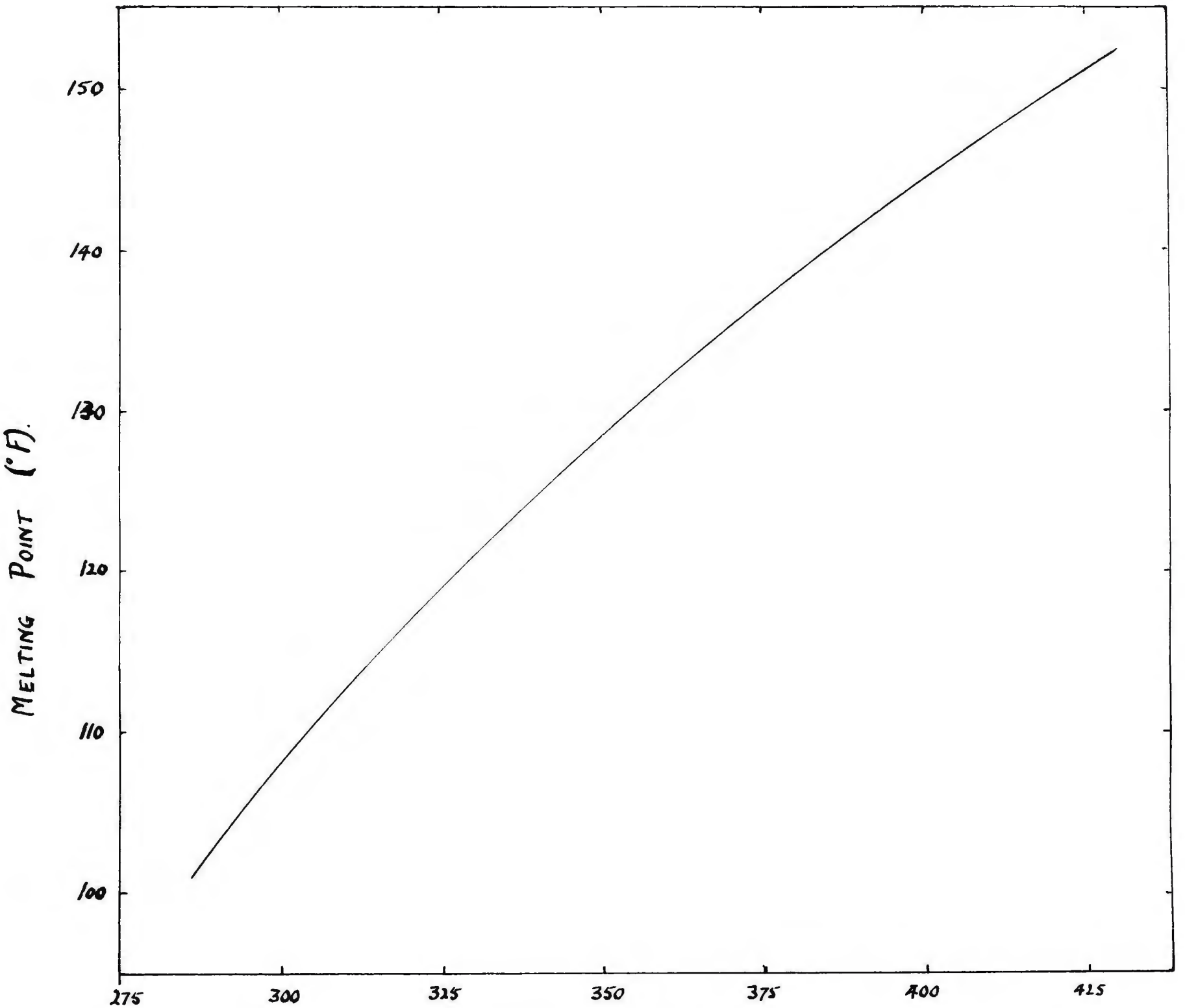

150
140
130
120
110
100
MELTING POINT (°F).
275
300
325
350
375
400
425
MOLECULAR WEIGHT.

FIG. 18.

In practice, the main calculation may be eliminated by obtaining the values from the graph of T versus M shown in Fig. 18 opposite and drawn from the following corresponding values of T and M.

TABLE XV.

^{o}K (T)	310.78	316.33	321.89	327.44	333.00	338.55
^{o}C.	37.78	43.33	48.89	54.44	60.00	65.55
^{o}F.	100	110	120	130	140	150
M.	283.5	304.5	328.3	354.9	385.3	421.0

Using this equation, the melting points of the wax blends reported by Berne-Allen and Work (Table XI Page 60.) have been calculated. Agreement between experimental and calculated values is excellent; the blend of melting point 56.9^{o}C. has the same calculated value, whilst the calculated value for the blend of melting point 59.1^{o}C. is 59.05^{o}C. It should be stressed, however, that such excellent agreement must not be anticipated in all cases.

DETERMINATION OF THE EQUILIBRIUM DIAGRAM.

Wax Stock.

The wax stock employed was a blend consisting of equal weights of four completely refined Anglo-Iranian waxes of the following melting points :- 130.95°, 127.85°, 119.85° and 108.35°F. The resulting blend of melting point 122.1°F., was used in all experiments from this stage.

Melting Point Method.

The I.P.T. Setting Point Method (Serial Designation P.S. 11a) was not used owing to the comparatively large amount (10 gms.) of the sample necessary for the determination. The method was therefore modified so that only 5 gms. were required. The simple apparatus is identical with that used for cloud-point determination (Fig. 6. P.24a) except that a stirrer is not employed. A glass test-tube, (length 8", diameter ¾") is filled to a mark (1½" from bottom) with the wax sample and placed in an air-jacket consisting of a larger glass boiling tube (length 6", diameter 1½") which, in turn, is placed in a 3-litre beaker containing water at a temperature 10 - 15°F. lower than the expected melting point of the sample. An N.P.L. Standard I.P.T. Wax Setting Point Thermometer is placed in the molten sample giving the set-up (without stirrer) shown in Fig. 6. A cooling curve is then plotted, the temperature being taken at half-minute intervals, starting when the wax is at a temperature 5°F. above its melting point, and continuing until the first minimum cooling

rate has been passed.

The melting point is taken as the temperature at which five or more identical consecutive readings are observed. All precautions mentioned in the I.P.T. method regarding the heating of the sample are observed.

The method gives duplicate results differing by not more than 0.05°F. The following are the figures for two typical duplicate sets of cooling curves :-

TABLE XVI.

WAX A.		WAX B.	
137.4	137.2	117.2	117.1
136.6	136.5	116.6	116.5
135.8	135.7	115.9	115.8
135.1	135.0	115.3	115.3
134.5	134.2	114.7	114.7
133.8	133.6	114.2	114.2
133.3	133.0	113.7	113.7
132.8	132.5	113.3	113.3
132.3	132.1	113.1	113.1
132.0	131.9	112.9	112.95
131.8	131.7	112.7	112.8
131.7	131.6	112.6	112.65
131.6	131.5	112.6	112.5
131.5	131.45	112.55	112.5
131.45	131.45	112.5	112.5
131.45	131.45	112.5	112.5
131.45	131.45	112.5	112.5
131.45	131.45	112.5	112.5
131.45 (9 mins.)	131.4	112.5	112.5
131.35 (13 mins.)	131.4	112.45	112.45
Bath Temp. 120°F.	Bath Temp. 115°F.	Bath Temp. 98°F.	Bath Temp. 101°F.
M. Pt. 131.45°F.	M. Pt. 131.45°F.	M. Pt. 112.5°F.	M. Pt. 112.5°F.

The melting point of wax is therefore defined as the temperature at which molten paraffin wax, when allowed to cool under the conditions specified above, first shows the minimum rate of temperature change.

On occasion, insufficient wax was available for the above method to be used. In such instances the wax was placed in a smaller test-tube which was then inserted in the 8" x $\frac{3}{4}$" test-tube, and the above procedure followed. By maintaining the bath temperature at 5°F. lower than the melting point of the sample a cooling curve was obtained which gave three identical consecutive readings. The melting point determined in this manner did not differ by more than 0.05°F. from the melting point obtained when using the larger sample.

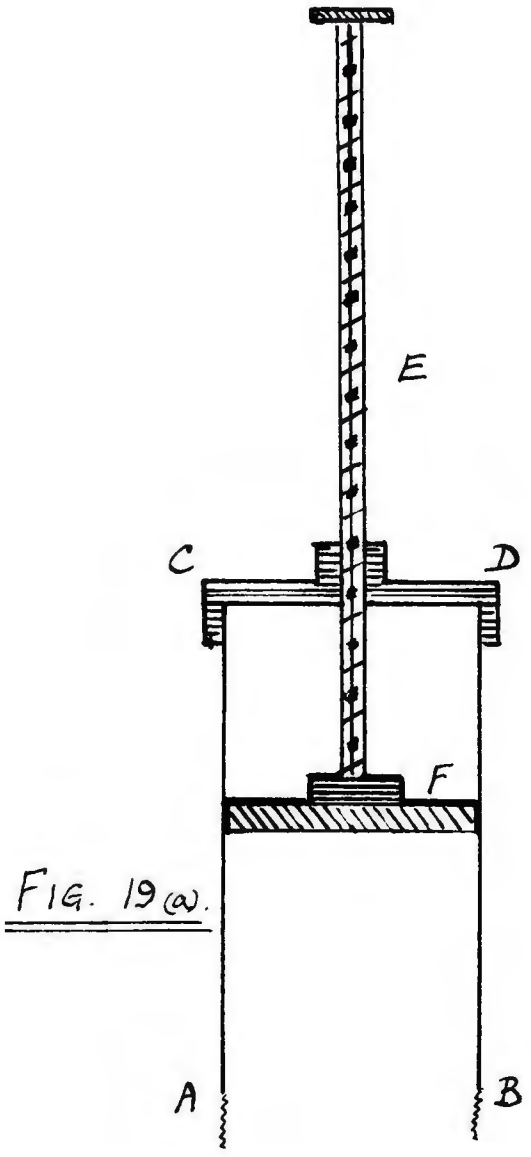
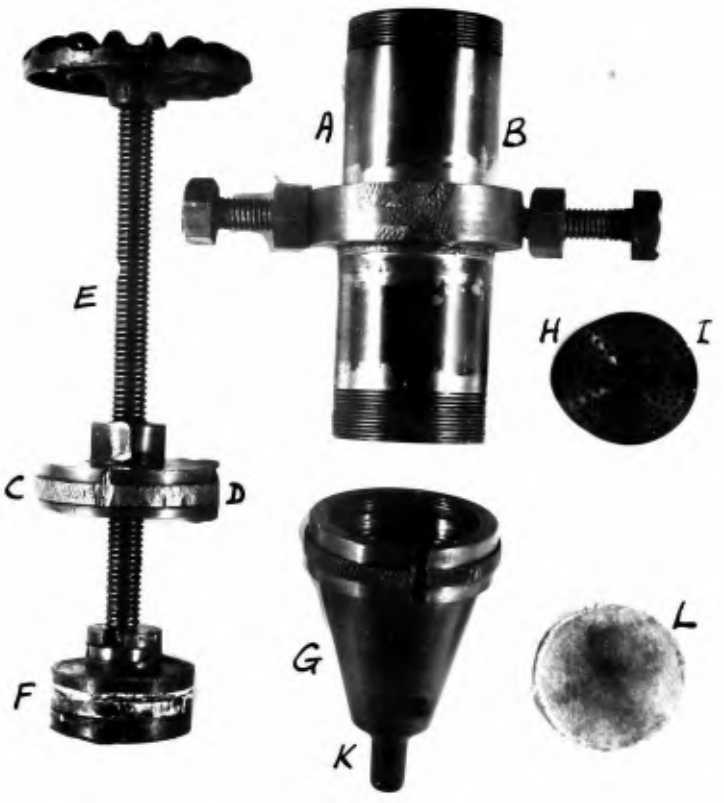


FIG. 19(a).



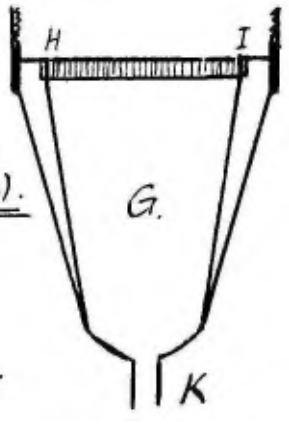


FIG. 19(b).

Modified Apparatus for Equilibrium Experiments.

The apparatus used for the determination of the equilibrium curve of the wax is illustrated in Figs. 19(a) and 19 (b) and in the photograph opposite.

Constructed in brass in order to avoid difficulties due to corrosion when standing in contact with the Thermostat water, it consists essentially of three sections :-

(1) The cylinder AB of diameter 5 cms. and length 14 cms. which is screwed into

(2) the cylinder head CD, through which passes the screw E carrying the piston head F, shown in Fig. 19(a),

and

(3) the conical cylinder head G, shown in Fig. 19(b)

The piston F consists of a brass plate with a rubber washer, the purpose of the latter being to prevent seepage of the liquid phase between the piston and the cylinder wall. A leather washer was employed initially, but considerable difficulty was experienced owing to loss of liquid phase in this manner. The small amount of "lost" phase collecting in the space between the under-part of the piston and the cylinder head CD, was found to have a melting point the same as that of the liquid phase formed in the experiment, and it was therefore concluded that seepage occurred during the separation of the liquid and solid phases (the method of separation will be

described later). This was confirmed by allowing liquid wax to stand for twelve hours in the part of the apparatus shown in Fig. 19(a), when it was found that no seepage had occurred during this time.

The conical cylinder head G contains a perforated brass filter plate HI of diameter 4.7 cms. and thickness 4 m.m., on which is placed a layer of thin canvas which, in turn, is covered with a layer of filter paper. This means of separating the liquid from the solid phase proved to be very satisfactory. The liquid passing through the filter plate was collected in a Buchner flask attached to the conical cylinder head by means of a rubber bung at K.

All screw connections were made water-tight by the use of Mobilgrease Water Pump Grease No. 6.

Experimental Procedure.

The portion of the apparatus shown in Fig. 19(a) was placed in the Thermostat (described on P. 26.), and was maintained in a vertical position by means of a cradle support attached to the inside of the bath. The molten wax sample of 70 - 80 gms. was then poured from a glass beaker into the cylindrical section of the apparatus. The liquid was stirred occasionally during the initial stages of cooling, but stirring was almost continuous from the time solid phase made its first appearance until the liquid/solid wax mixture had cooled to the temperature of the Thermostat. After reaching the Thermostat temperature, the

mixture was allowed to stand for a further six hours, during which time stirring was intermittent.

At the end of this period the conical cylinder head with Buchner flask attached was screwed into position at AB. The apparatus was then completely immersed in the Thermostat and allowed to remain in this position for one hour, in order to allow the complete apparatus to attain the temperature of the bath.

The apparatus was then momentarily taken from the Thermostat, inverted, and immediately replaced in the cradle support which had been so designed that the whole apparatus (except for a portion of the lead screw E) was immersed whilst being supported in this position.

Pressure was then applied to the solid/liquid equilibrium mixture by slowly turning the screw E. This procedure was continued until it was found impossible to turn the screw further, at which point the separation of the two phases was assumed to be complete. This operation continued over a period of 30 - 45 minutes, but the apparatus was allowed to remain in the Thermostat for a further period of two hours, during which time the screw E was maintained in the position of maximum pressure. The apparatus was then taken from the Thermostat, the Buchner flask containing the liquid phase removed from the conical cylinder head G, and the conical head separated from the cylinder by disconnecting at AB.

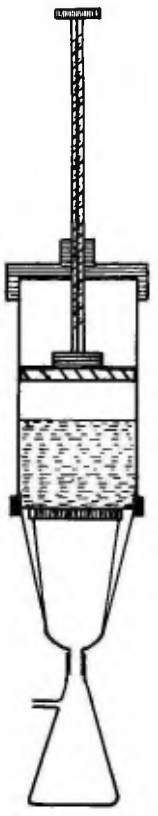


Fig 20(a).

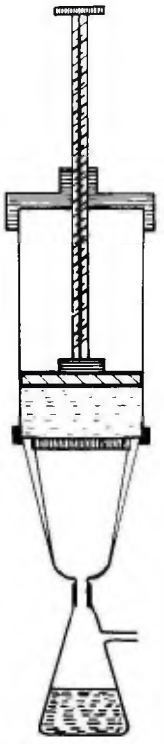


Fig. 20(b).

FIGS. 20(a) & 20(b).

The solid phase was removed from the cylinder as a solid block by turning the screw E. A small amount of the solid phase adhered to the top of the piston but this was easily and completely removed by scraping with a thin nickel spatula. The total solid phase was then weighed and its melting point determined.

The amount of liquid phase was determined by weighing the Buchner flask before and after the experiment. It was found that the canvas filter sometimes increased in weight during the experiment by as much as 0.75 gm. This was undoubtedly due to absorption of some of the liquid phase and the canvas was therefore weighed before and after each experiment and a correction applied to the weight of the liquid phase. A new (or cleaned) canvas filter was used in each experiment.

Figs. 20(a) and 20(b) illustrate respectively the set-up of the apparatus - (a) immediately preceding the separation of the two phases, and (b) on completion of the separation.

Construction of the Equilibrium Diagram.

Two series of experiments were necessary for the construction of the equilibrium diagram, (a) for the determination of the solidus-liquidus curves representing a one-stage separation of the two phases, and (b) for the determination of the solidus-liquidus curves representing a multi-stage removal of the liquid phase - the approach to the equilibrium diagram applicable to the process of fractional melting.

(a) One-stage removal of liquid phase.

The solidus-liquidus curves representing this process were determined at various temperatures covering the melting range of the wax stock using the procedure outlined on Pages 78-80. In each experiment, the yields and melting points of the solid and liquid phases were determined. In many cases the corresponding cloud-points were also found, and it will be noted that the difference between melting point and cloud-point varies from 0.05°F. to 0.15°F. Thus, the error introduced by using cloud-point instead of melting point is not large and the generalisations made from the results of the preliminary experiments, in which cloud-point was used to characterise the wax fractions, are therefore quite justified.

Experimental results are given in Table XVII (Page 82).

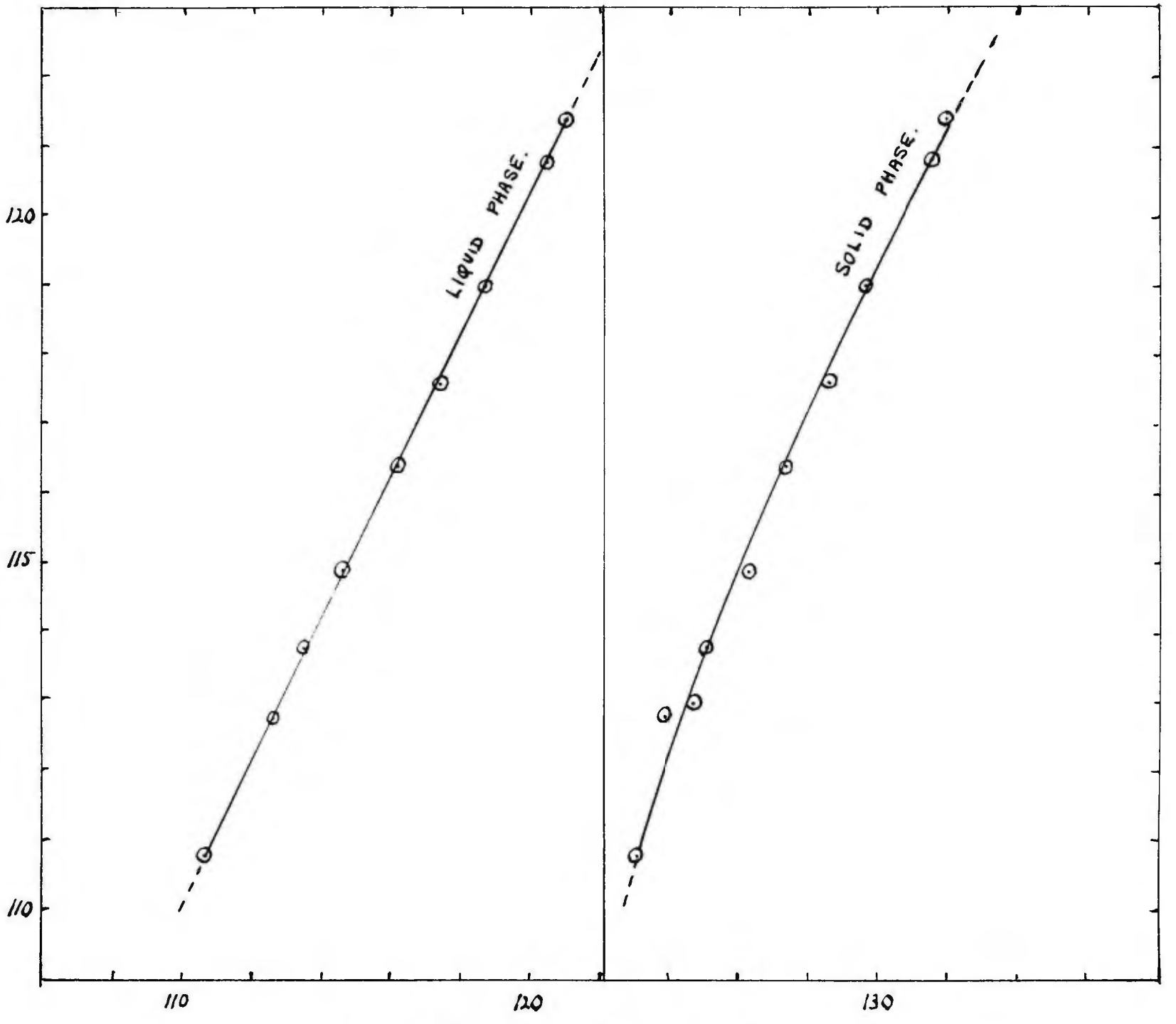

LIQUID PHASE.
SOLID PHASE.
120
115
110
110
120
130
EQUILIBRIUM TEMPERATURE (°F).
MELTING POINT (°F).

FIG. 21.

TABLE XVII.

Expt. No.	Equil. Temp. (°F.)	% by Weight.		Melting Point (°F.)		Cloud Point (°F.)	
		Solid Phase	Liquid Phase	Solid Phase	Liquid Phase	Solid Phase	Liquid Phase
1.	110.8	92.1	7.9	123.1	110.6	123.15	-
2.	112.8	82.1	17.9	123.9	112.55	124.0	112.65
3.	113.0	77.4	22.6	124.7	112.65	-	-
4.	113.8	72.8	27.2	125.15	113.45	-	-
5.	114.9	61.1	38.9	126.25	114.55	126.3	114.6
6.	116.4	52.0	48.0	127.3	116.15	127.35	116.2
7.	117.6	40.9	59.1	128.6	117.35	128.65	117.45
8.	119.0	30.4	69.65	129.65	118.65	129.7	-
9.	120.8	13.3	86.7	131.55	120.5	131.6	120.6
10.	121.4	8.6	91.4	131.95	121.05	-	121.1

The results are shown graphically in Fig. 21 opposite.

From the melting points of the solid and liquid phases obtained in each experiment, the yield of solid phase was calculated

(a) using the relation $T = \frac{414.5\ M}{M + 94.4}$

(b) on the assumption that melting point is additive.

Comparative figures are given in Table XVIII (Page 83).

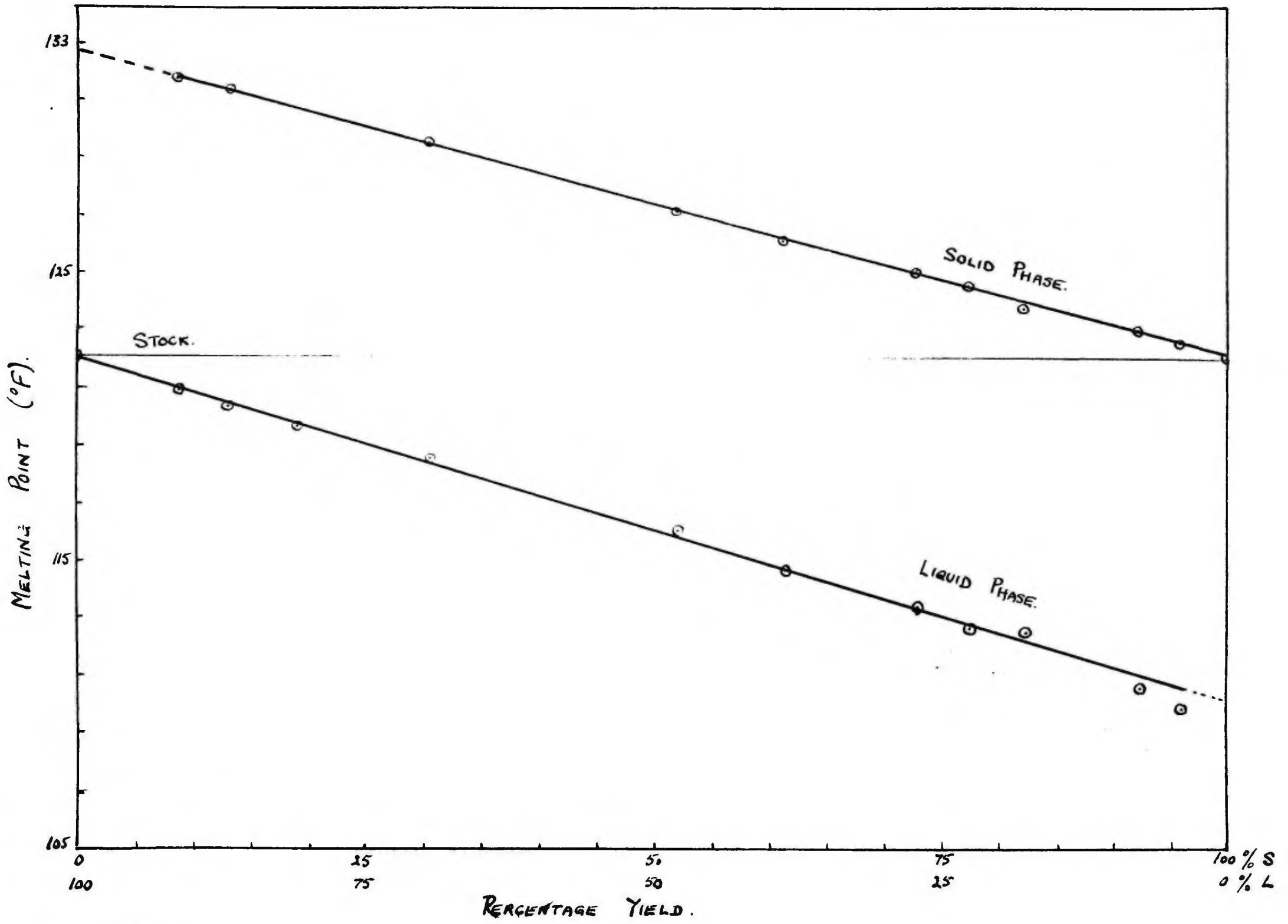

133
125
115
105
Melting Point (°F).
Stock.
Solid Phase.
Liquid Phase.
0
100
25
75
50
50
75
25
100 % S
0 % L
Percentage Yield.

FIG. 22.

TABLE XVIII.

Expt. No.	YIELD - % by WEIGHT: Actual	Calculated from $T = \frac{414.5M}{M+94.4}$	Experimental - Calculated	Calculated from Melting Point	Experimental - Calculated
1.	92.1	91.4	+ 0.7	92.0	+ 0.1
2.	82.1	83.0	- 0.9	84.1	- 2.0
3.	77.4	77.4	± 0.0	78.4	- 1.0
4.	72.8	72.7	+ 0.1	73.9	- 1.1
5.	61.1	62.4	- 1.3	64.5	- 3.4
6.	52.0	51.1	+ 0.9	53.4	- 1.4
7.	40.9	40.4	+ 0.5	42.2	- 1.3
8.	30.4	29.8	+ 0.6	31.4	- 1.0
9.	13.3	13.3	± 0.0	14.5	- 1.2
10.	8.6	9.1	- 0.5	9.6	- 1.0

It is clear that agreement between the actual and calculated yields is closer when the relation $T = \frac{414.5\ M}{M + 94.4}$ is used for the calculation of the latter. The use of this relation is therefore justified, but at the same time, it will be noted that there is no very serious discrepancy between the actual and calculated values when the latter are obtained on the assumption that melting point is additive.

The yield/melting point graph for the two phases is given in Fig. 22 opposite, from which it is seen that the yield

is a linear function of the melting point. For yields of the liquid phase lower than 10% the melting point is slightly lower than indicated by the linear relationship, and it is suggested that this is due to the presence in the wax stock, of a small amount of oil, probably contained initially in the wax of melting point 108.35°F. Assume, for example, that the original 108.35° melting point wax contains 1% oil. The oil content of the wax stock, which contains 25% of this particular wax, is therefore 0.25%. Now it is likely that whatever the yield of liquid phase, most of the oil would be present in this phase due to the press method employed for the separation of the phases. Thus, liquid phase obtained from an equilibrium experiment in 5% yield would contain approximately $0.25 \times \frac{100}{5} = 5\%$ oil. By comparison with data given in Fig. 9 (Page 30A) it is clear that the presence of this amount of oil would explain this deviation from the linear relation. With higher yields of liquid phase, the oil/wax ratio decreases, and the effect of the oil on the melting point becomes less pronounced, until at 20% yield it is negligible, and the linear relationship then holds.

Two-stage removal of liquid phase.

Before proceeding with the experiments on the multi-stage removal of liquid phase, two two-stage experiments were conducted.

(1) Solid phase of melting point 126.25°F. (ex Expt. 5 Table XVII) after reaching equilibrium at 119.8°F.,

gave 64.7% solid phase of melting point 129.6°F., and 35.3% liquid phase of melting point 119.55°F.

The yield of solid phase based on original stock = $\frac{64.7 \times 61.1}{100}$ = 39.5%.

(cf 30.5% yield of solid phase of same melting point from one-stage process - Fig. 22).

(b) Solid phase of melting point 127.3°F. (ex Expt. 6 Table XVII). after reaching equilibrium at 119.8°F. gave 73.9% solid phase of melting point 129.7°F., and 26.1% liquid phase of melting point 119.65°F.

The yield of solid phase based on original stock = $\frac{73.9 \times 52.0}{100}$ = 38.4%.

(cf 29.5% yield of solid phase of same melting point from one-stage process - Fig. 22).

These experiments confirm the findings of the preliminary work - a two-stage removal of liquid phase results in a higher yield of lower melting point solid phase than that obtained in a one-stage removal at the higher of the two equilibrium temperatures.

(b) Multi-stage (14-stage) removal of liquid phase.

98 gms. of the wax stock were placed in the apparatus and allowed to attain equilibrium at a temperature slightly above the point of complete solidification of the wax (see Fig. 21) and such that the equilibrium mixture contained approximately 95% solid phase. After equilibrium had been attained the experiment was completed as previously described.

The liquid phase was allowed to solidify in the Buchner flask and was then removed with a nickel spatula. Last traces were removed from the flask with petroleum ether. The solvent was evaporated and the traces of wax remaining, added to the bulk of the liquid phase.

The solid phase was removed from the apparatus, weighed, its melting point determined, liquefied and replaced in the apparatus. The Thermostat was then set at a slightly higher temperature such that approximately 10% liquid was present in the equilibrium mixture. After reaching equilibrium, the solid and liquid phases were separated in the usual manner and treated as described above. This process was repeated until the quantity of solid remaining became so small that it was impossible to continue further. In all, fourteen separations were made. Essential figures for each of the fourteen experiments are given in Table XIX (Page 87).

TABLE XIX.

Expt. No.	Equil. Temp.	Wt.solid phase taken	SOLID PHASE			LIQUID PHASE		
			Weight (gms.)	%	Melting Point	Weight (gms.)	%	Melting Point
1.	110.2	97.95	93.65	95.6	122.75	4.3	4.4	109.85
2.	111.0	92.27	89.82	97.4	123.05	2.45	2.6	-
3.	112.7	88.68	84.18	94.9	123.5	4.50	5.1	112.55
4.	114.1	82.23	71.56	87.0	124.85	10.67	13.0	113.85
5.	115.8	70.42	61.80	87.8	126.05	8.62	12.2	115.5
6.	117.1	60.58	54.48	89.9	126.95	6.06	10.1	116.9
7.	118.7	52.11	45.72	87.7	128.2	6.39	12.3	118.45
8.	120.0	43.66	39.53	90.5	129.1	4.13	9.5	119.7
9.	121.5	38.68	33.75	87.2	130.1	4.93	12.8	121.25
10.	123.5	32.85	26.40	80.3	131.5	6.45	19.7	123.25
11.	125.2	25.71	20.11	78.2	133.1	5.60	21.8	124.9
12.	126.7	17.53	14.46	82.5	134.2	3.07	17.5	126.5
13.	128.9	13.87	8.91	64.2	136.35	4.96	35.8	128.6
14.	132.4	8.67	4.96	57.2	138.6	3.71	42.8	132.1

The percentage yield of solid phase based on 100% original wax stock may be calculated from the figures given in column 4 above. On this basis, the percentage yield of solid phase of melting point 123.5°F., for example, is $95.6 \times \frac{97.4}{100} \times \frac{94.9}{100} = 88.4\%$ etc.

The experiments described above are not sufficient for the construction of the complete diagram for the 14-stage process,

as no information is given concerning the melting points of the ~~bulked~~ blended liquid phases.

For example, at the completion of experiment 3, 88.4% of the original stock remained as solid phase and the 11.6% liquid phase had been removed in three fractions, the melting point of each of these fractions having been determined separately. A knowledge of the melting points of the ~~bulked~~ blended liquid fractions is essential, and the liquid fractions were therefore re-blended in their equivalent amounts and the melting point of each blend determined.

Results are given in column 5 of Table XX below, in which are also recorded the yield and melting point of the corresponding solid.

TABLE XX.

	SOLID PHASE		LIQUID PHASE	
Expt. No.	Yield %	Melting Point	Yield %	Melting Point
-	100.0	122.1	0.0	-
1.	95.6	122.75	4.4	109.85
2.	93.1	123.05	6.9	110.25
3.	88.4	123.5	11.6	-
4.	76.9	124.85	23.1	112.55
5.	67.5	126.05	32.5	-
6.	60.7	126.95	39.3	114.05
7.	53.3	128.2	46.7	-
8.	48.2	129.1	51.8	115.30
9.	42.1	130.1	57.9	-
10.	33.8	131.5	66.2	116.95
11.	26.4	133.05	73.6	-
12.	21.8	134.2	78.2	118.35
13.	14.0	136.35	86.0	-
14.	8.0	138.6	92.0	120.4
-	0.0	-	100.0	121.95

The melting point of the 100% liquid phase should, of course, be 122.1°F. - that of the original wax stock - and considering the number of steps involved in its determination, the actual figure of 121.95°F. obtained for the re-blended stock is very satisfactory.

As the yields of both phases and the melting point of the solid phase are known, the melting points of the various ~~bulked~~ blended liquid phases could be calculated by applying the equation $T = \frac{414.5M}{M+94.4}$.

As a further test of the applicability of this relation, the yields of the phases were calculated in this manner from the known melting points. The yields calculated on the assumption that melting point is additive are also given, and the comparison of the figures for the solid phases, given in Table XXI below, again justifies the use of the equation.

TABLE XXI.

	YIELD - % by WEIGHT				
Stage No.	Actual	Calculated from $T = \frac{414.5M}{M+94.4}$	Experimental - Calculated	Calculated from Melting Point	Experimental - Calculated
4.	76.9	76.5	+ 0.4	77.6	- 0.7
6.	60.7	60.7	± 0.0	62.4	- 1.7
8.	48.2	48.0	+ 0.2	49.3	- 1.1
10.	33.8	34.1	- 0.3	35.4	- 1.6
12.	21.8	23.3	- 1.5	23.6	- 1.8
14.	8.0	8.6	- 0.6	9.3	- 1.3

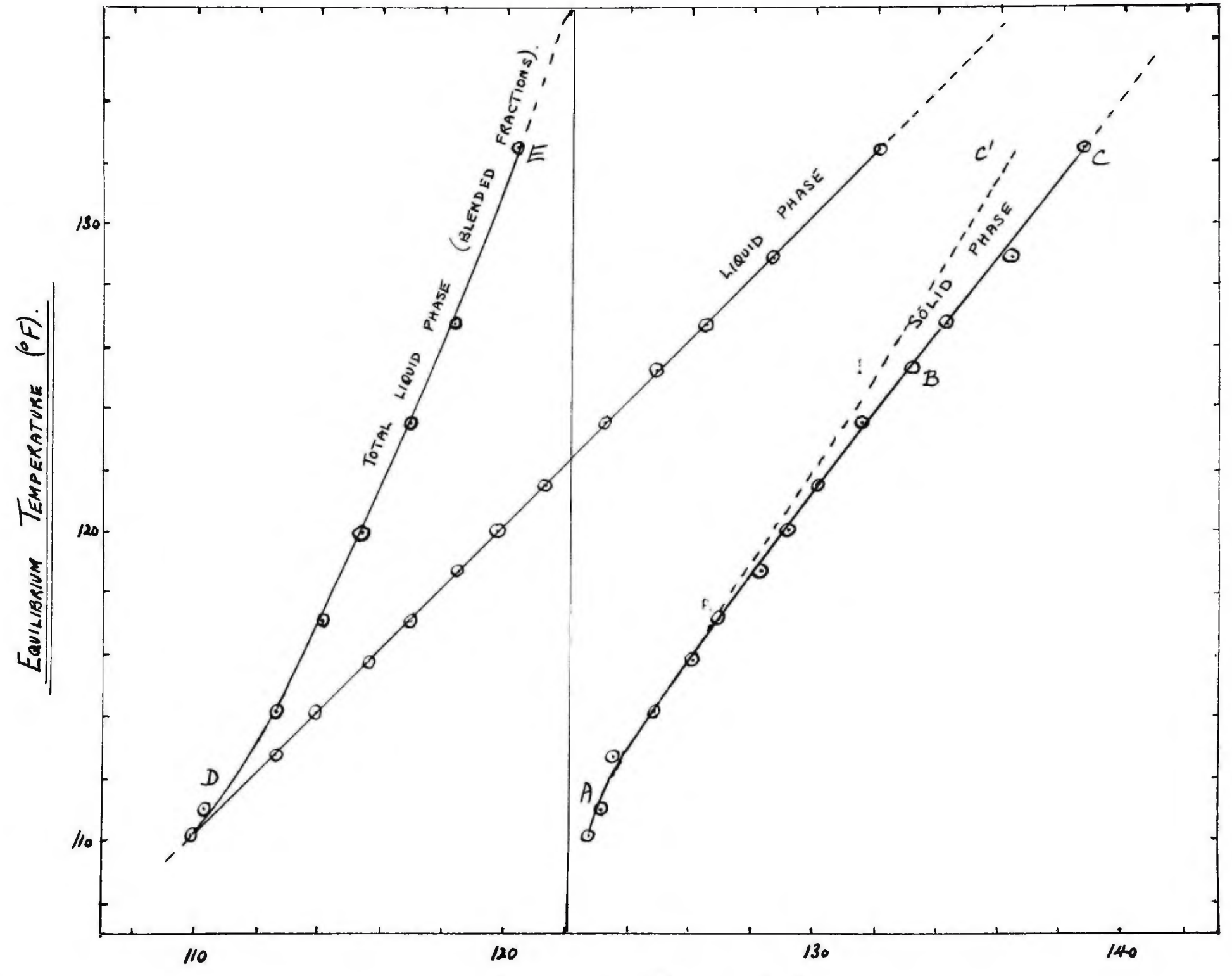

EQUILIBRIUM TEMPERATURE (°F).
130
120
110
TOTAL LIQUID PHASE (BLENDED FRACTIONS).
III
LIQUID PHASE
C'
SOLID PHASE
C
B
D
A
110
120
130
140
MELTING POINT (°F).

FIG. 23.

Liquidus-Solidus Curves for 14 - Stage Process.

The curves plotted from the data contained in Tables XIX and XX are shown in Fig. 23 opposite. Before discussing the diagram in detail, a preliminary indication of its limitations must be given.

It has been stated previously that the equilibrium diagram for a 14-stage removal of liquid phase can represent only an approach to the diagram for the infinite-stage, or ideal, process. Further reasons for this will now be considered :-

(a) It is known that the last traces of a solvent cannot be removed from wax by a pressing operation alone and that special means, - for example, passing a stream of nitrogen through the molten sample - must be employed. It is probable, therefore, that a small amount of liquid wax is retained by the solid phase at each stage. Unfortunately, there seems to be no satisfactory way of estimating the extent of this retention.

(b) Errors are incurred by removing the liquid phase in approximately 10%, instead of in infinitesimally small, fractions. The greatest error occurs from stage 10 to stage 14 (see Table XIX Column 8) where, owing to the comparatively small amount of wax remaining, it was found necessary to remove the liquid phase in quantities increasing from 20% to 43% of the equilibrium sample in order to obtain sufficient material for a melting point determination. The effect on the melting point of the solid phase caused by 10% and 40% removals of liquid phase is indicated

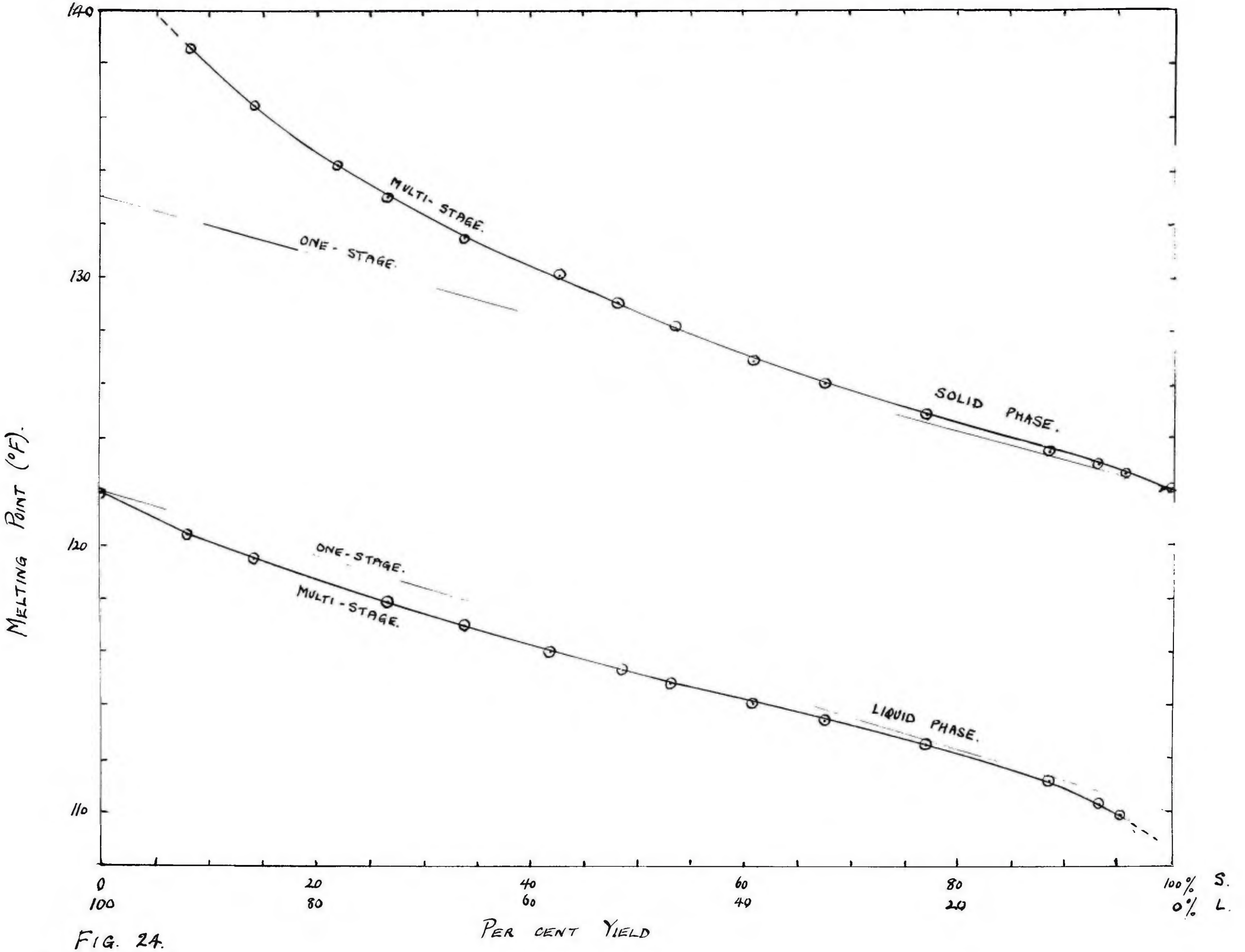

140
130
120
110
MELTING POINT (°F).
MULTI-STAGE.
ONE-STAGE.
SOLID PHASE.
ONE-STAGE.
MULTI-STAGE.
LIQUID PHASE.
0
100
20
80
40
60
60
40
80
20
100% S.
0% L.
PER CENT YIELD

FIG. 24.

from the data for the one-stage process (see Table XVII Page 82), although in the experiments now under consideration the difference will not be so great owing to the narrower melting range of the wax present at stage 10.

It is suggested, therefore, that the solidus curve for the infinite-stage or ideal process would be displaced from the solidus curve ABC in the manner indicated by the curve A'B'C' (Fig. 23) - the greater deviation being shown in the region B'C' corresponding to stages 10-14. The liquidus curve DE would be displaced similarly. Thus, as a higher equilibrium temperature is necessary in the 14-stage than in the one-stage process to obtain a solid phase of given melting point, so in the ideal process the equilibrium temperature will be even higher. Also, as the melting point of the last traces of solid phase obtained in the 14-stage process is higher than the corresponding melting point for a one-stage process, so the last traces of solid phase obtained in the ideal process will be of even higher melting point.

The yield/melting point curves for the 14-stage process and the corresponding curves for the one-stage process (see Fig. 22 Page 83a) are given in Fig. 24 opposite. Comparison of the two curves for the respective solid phases shows that

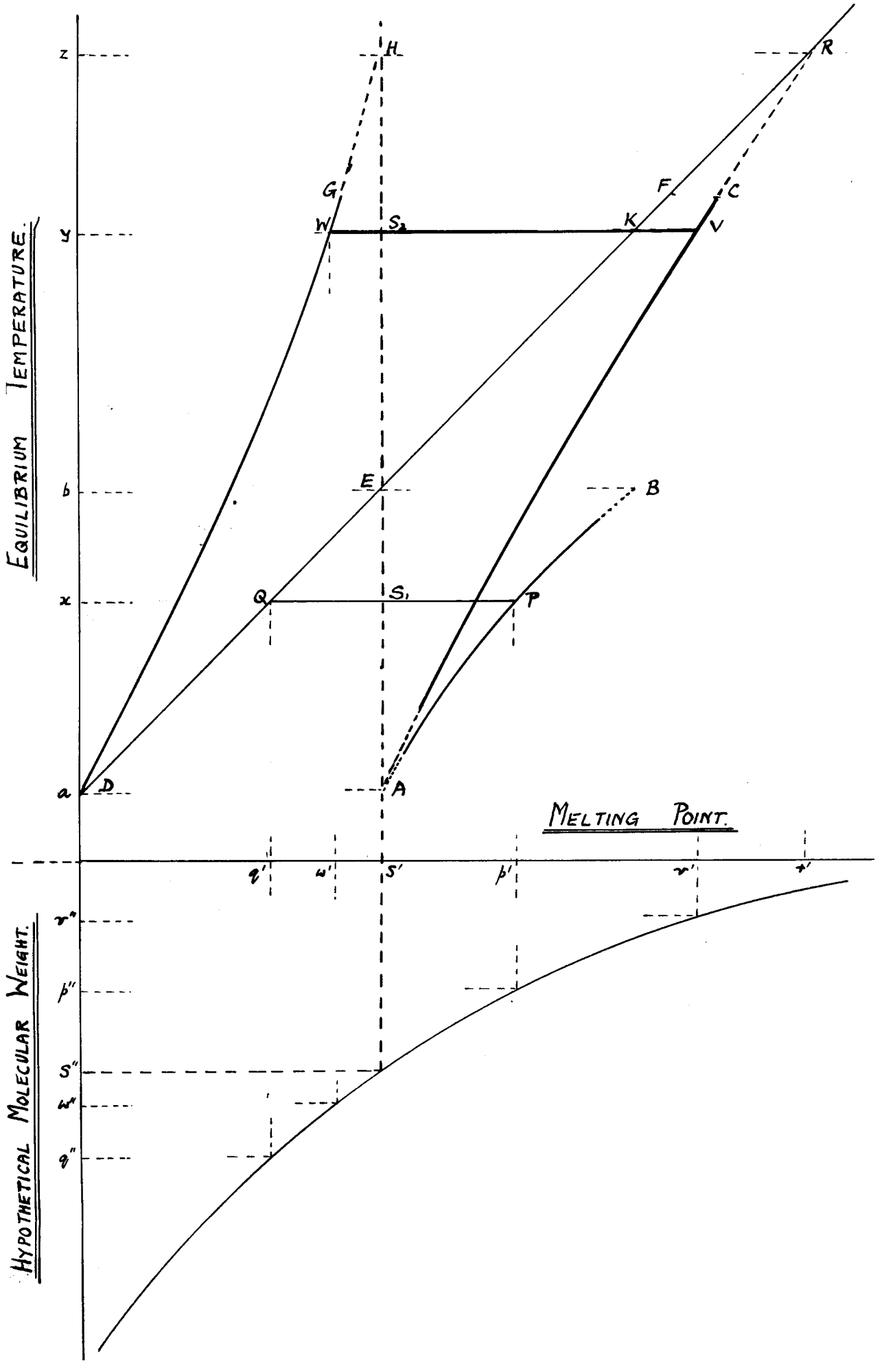
(a) the yield of solid of any given melting point, within the range possible, is higher in the 14-stage than in

the one-stage process, and

(b) waxes of higher melting point are obtainable in the 14-stage process.

The above findings confirm the inferences from the preliminary work.

FIG. 25.


EQUILIBRIUM TEMPERATURE.
z
y
b
x
a
H
G
W
S₂
K
F
C
V
R
E
B
Q
S₁
P
D
A
MELTING POINT.
q'
w'
S'
p'
r'
t'
HYPOTHETICAL MOLECULAR WEIGHT.
r''
p''
S''
w''
q''

Consideration of the Complete Equilibrium Diagram.

A more detailed study will now be made of the complete equilibrium diagram which is both qualitatively and quantitatively applicable to the process of fractional melting for the separation of waxes of different melting points from a given oil-free wax stock. The complete diagram shown in Fig. 25 opposite, is based essentially on Fig. 23 (Page 90a), Fig. 21 (Page 82a) and Fig. 18 (Page 73a). This will be considered sectionally.

Curves AB and DE.

AB and DE represent the solidus and liquidus curves applicable to a one-stage separation of the two phases at any temperature within the limits of their co-existence.

AH is the stock line, the wax stock having a melting point of (S') corresponding to a hypothetical molecular weight of (S"). The temperature (a) corresponding to A represents the point at which the stock just begins to melt when heated. It is completely liquid at temperature (b) corresponding to B. This temperature range (b) - (a) therefore represents the melting range of the stock. In this connection, it is necessary to distinguish between the melting range of the stock and the melting ranges of the constituent waxes.

It is found by experiment that the liquid phase has, in general, a melting point 0.2° - 0.3°F. lower than the equilibrium temperature. The liquidus curve DE may therefore be considered

as a straight line only slightly removed from the 45° line. These curves may be applied quantitatively in the following manner. Let the stock represented by point S_1 attain equilibrium at any temperature (x) within its melting range. The equilibrium mixture consists of solid and liquid phases represented respectively by the points P and Q on the solidus and liquidus curves, and having melting points of (p') and (q') and hypothetical molecular weights of (p") and (q") respectively. The relative amounts of solid and liquid phases at this temperature, $QS_1 : PS_1$, are calculated from the relation (s")-(q") : (p")-(s"), from which

$$\text{Yield of solid phase} = \frac{(s")-(q")}{(p")-(q")} \times 100\%$$

$$\text{and yield of liquid phase} = \frac{(p")-(s")}{(p")-(q")} \times 100\%$$

Curves AC, DEF, and DG.

The curves AC, DEF, and DG relate to the infinite-stage or ideal process. Curve AC represents the change in melting point of the solid phase during infinitesimally small temperature increments, after each of which the resulting small amount of liquid phase is completely removed.

It was found in the 14-stage experiments that the melting point of the liquid phase at each removal stage was in general, 0.2°-0.3°F. lower than the equilibrium temperature. Hence, the change in melting point of the liquid phase is represented by DEF,

where DEF may be considered, within experimental error, as a straight line. The composition of the ~~bulked~~ blended liquid phases is given by curve DG, and this curve therefore gives the melting point of the total liquid phase corresponding to any solid phase represented on AC.

Applying these curves to this ideal process of fractional melting, it is clear that the solid phase changes in composition (characterised by melting point) along AC; the total liquid phase removed changes in composition along DG; whilst the composition of the liquid phase being removed at any stage of the process, is given by the curve DEF.

The theoretical yield of solid phase of any given melting point may be readily determined. Suppose the theoretical yield of solid phase of melting point (v') is required. This melting point is represented by V on the solidus curve AC. Now the liquid phase should be removed in an infinitely large number of stages over the temperature range (y)-(a), and the melting points of the phases removed cover the range from D to K.

The bulk liquid phase has a melting point corresponding to W on curve DG. The original stock is represented by the point S_2.

The yields of solid and liquid are calculated as in the one-stage removal :-

The ratio of solid to total liquid, $WS_2 : S_2V$, is given quantitatively by the relation $\left[(s'') - (w'')\right] : \left[(r'') - (s'')\right]$, from which

$$\text{Yield of solid} = \left[\frac{(s'') - (w'')}{(v'') - (w'')}\right] \times 100\%$$

$$\text{and yield of liquid phase} = \left[\frac{(v'') - (s'')}{(v'') - (w'')}\right] \times 100\%$$

Significance of points R and H.

In reference to the equilibrium diagram given by two substances forming a continuous series of solid solutions, it has been shown, theoretically, that during the ideal process of fractional melting of any mixture of the two components, the composition of the solid phase continuously approaches that of the pure component of higher melting point until, in the limit, the last trace of solid remaining consists of this pure component (Page 18).

From the nature of the curves AC and DEF (Fig. 25) it is suggested that with wax mixtures also, the ideal process of fractional melting, if carried to completion, will lead to a trace of solid phase consisting of a pure compound. If this is the case, the solidus and liquidus curves, AC and DEF respectively, will meet at some point R as, for a pure compound, liquid and solid of the same composition co-exist in equilibrium at the melting point. Thus, in the limit - represented by point R - the melting points

of the solid and liquid phases, and also the equilibrium temperature, are identical.

In this case the melting point of the liquid phase is not, of course, 0.2 - 0.3°F. lower than the equilibrium temperature, as is normally found in the equilibrium experiments described. However, it will be appreciated that the definition of melting point on which this work is based is not strictly applicable to a pure compound. The melting point of a pure compound may be defined as that temperature at which solid and liquid phases of the same composition co-exist in equilibrium, that is, the temperature at which solid first appears in the liquid when the latter is cooled. This temperature must therefore be identified with the equilibrium temperature associated with the equilibrium experiments on wax mixtures.

The point H at which the curve DG meets AH corresponds to the point R. At the stage represented by R, only a trace of solid phase remains, and it may be assumed that the liquid phase removed represents 100% of the original wax stock. Hence, the melting point of the ~~bulked~~ blended liquid fractions must be the same as that of the original stock, and the curve DG will therefore meet the stock line AH at the point H, representing the equilibrium temperature (z).

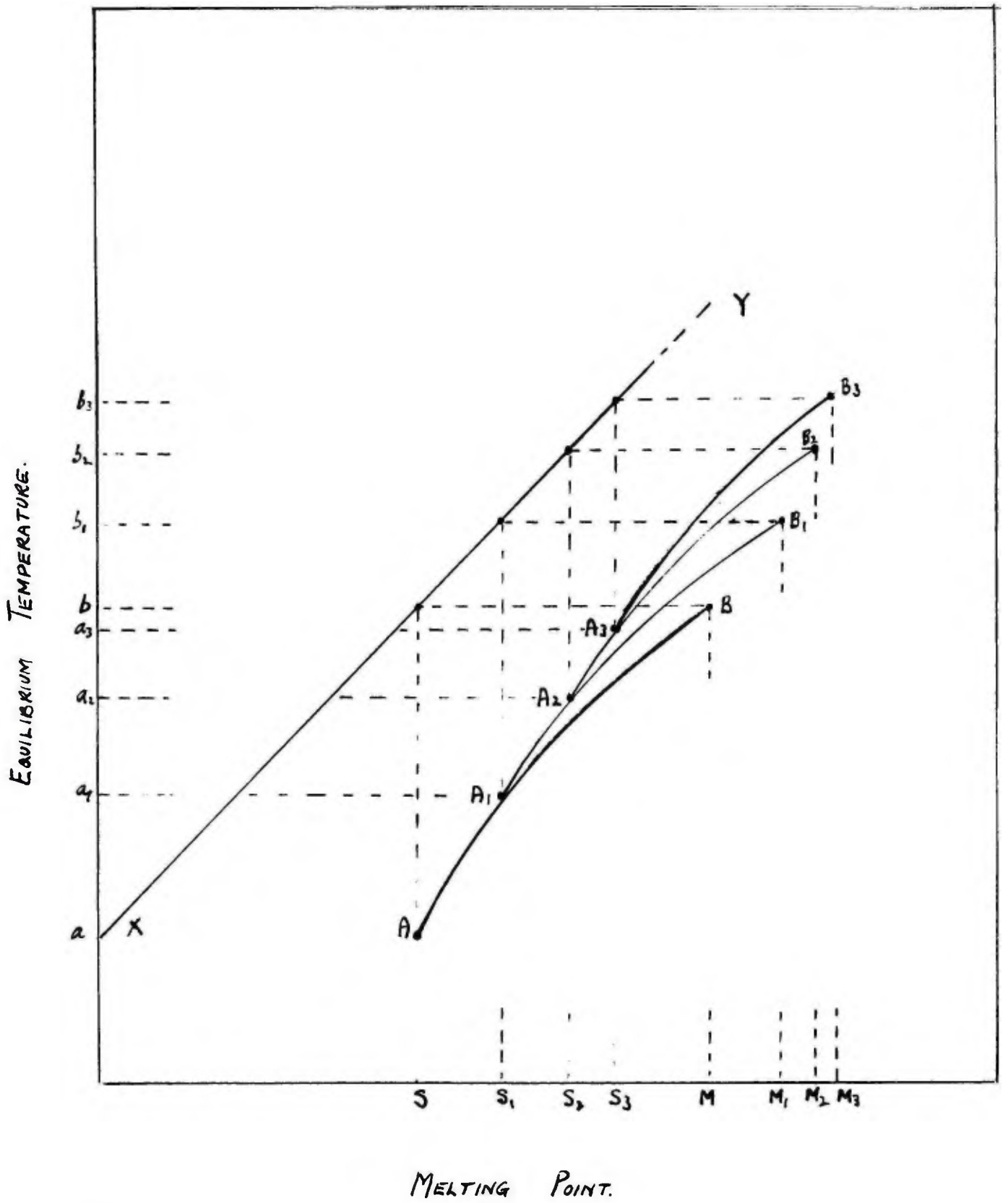

Y
b_3
b_2
b_1
b
a_3
a_2
a_1
a
X
A
A_3
A_2
A_1
B_3
B_2
B_1
B
S
S_1
S_2
S_3
M
M_1
M_2
M_3
EQUILIBRIUM TEMPERATURE.
MELTING POINT.

FIG. 26.

Theoretical significance of Solidus Curves AB and AC.

It will be recalled that in the equilibrium diagram (Fig. 4 Page 18a) for the two substances forming a continuous series of solid solutions, the solidus curve AB indicates the change in composition of the solid phase during the fractional removal of the liquid, irrespective of the number of stages in which the liquid is removed. It has been shown that the solidus curve AB (Fig. 25 Page 93a) in the wax equilibrium diagram relates to a one-stage removal only of liquid, and an attempt will now be made to explain this limited application.

In Fig. 26 opposite, AB and XY are the solidus and liquidus curves (corresponding to AB and DE in Fig. 25) applicable to equilibrium experiments involving a one-stage removal of liquid phase.

The wax stock is of melting point S and of melting range (b-a), where (b) is approximately 0.2°F. higher than S. The stock is completely liquid at the temperature (b), and M, corresponding to B, therefore represents the melting point of the highest melting wax (solid phase) obtainable from this stock in a one-stage equilibrium experiment.

Assume that the stock has attained equilibrium at a temperature (a_1) slightly higher than (a) and that the liquid phase has been completely removed. The solid phase remaining, represented by point A_1 on the solidus curve AB, will have a

melting point of S_1. Now this solid phase has a melting range of $(b_1 - a_1)$ and will be completely liquid at temperature (b_1). Also, it has been shown previously that a multi-stage removal of liquid phase results in a solid phase of higher melting point than that obtainable from a one-stage process. Hence, it may be assumed that the highest melting wax obtainable from A_1 will have a melting point slightly higher than M. Let this melting point be M_1. The point B_1 is therefore defined in reference to temperature (b_1) and melting point M_1.

It is now clear that the solidus curve AB will apply only to the original stock and that another curve having A_1 and B_1 as terminal points is necessary for the solid phase A_1. As the new stock A_1 does not differ greatly from A, the solidus curve A_1B_1 will be similar in form to the curve AB.

Now, allow solid A_1 to attain equilibrium at a temperature (a_2) slightly higher than (a_1), and again completely remove the liquid phase. The solid phase remaining, represented by point A_2 on the solidus curve A_1B_1, is of melting point S_2; its melting range is $(b_2 - a_2)$ and it is therefore completely liquid at the temperature (b_2). Also, the highest melting wax obtainable from A_2 by a one-stage removal of the liquid phase will be slightly higher in melting point than that obtainable from A_1. Let this be represented by M_2, thus completely defining the point B_2. Thus, the solidus curve A_1B_1 is not applicable to the solid phase A_2, and another curve A_2B_2, similar

in form to A_1B_1 and having A_2 and B_2 as the terminal points, is necessary.

Similarly for A_3, A_4, A_5.....

If the transitions from A to A_1, A_1 to A_2, A_2 to A_3, etc. are obtained by infinitesimally small temperature increments accompanied by the complete removal of the liquid phase at each stage, then the curve passing through A, A_1, A_2, A_3..... will represent the change in composition of the solid phase in the ideal process of fractional melting, and it will correspond to the curve AC in Fig. 25 (Page 93a).

Possibility of Constructing Equilibrium Diagram from limited Experimental Data.

It will be appreciated from the foregoing discussion, that the equilibrium diagram is of such a nature that the experimental difficulties involved in its determination are almost insuperable, and that despite all precautions, only an approach to the actual curve representing the change in melting point of the solid phase during the infinite-stage removal of liquid phase, may be obtained. The possibility of its construction by applying certain theoretical considerations (see Page 96-) in conjunction with a limited amount of experimental data was therefore considered, but unfortunately without success.

In reference to Fig. 25 (Page 93a), it is clear that the liquidus curve DEF may be inserted immediately on the assumption that the melting point of the liquid phase obtained in a one-stage equilibrium experiment is 0.2°F. lower than the equilibrium temperature. It has also been shown that for a one-stage process the yield/melting point relation for the two phases is linear (Fig. 22 Page 83a). This graph may therefore be obtained from the results of two or three experiments at different temperatures within the melting range of the stock. From the graph and the relation $T = \frac{414.5M}{94.4+M}$, the solidus and liquidus curves AB and DE (Fig. 25) respectively may be calculated.

Before any attempt may be made to construct the infinite-stage solidus curve AC (Fig. 25) from theoretical

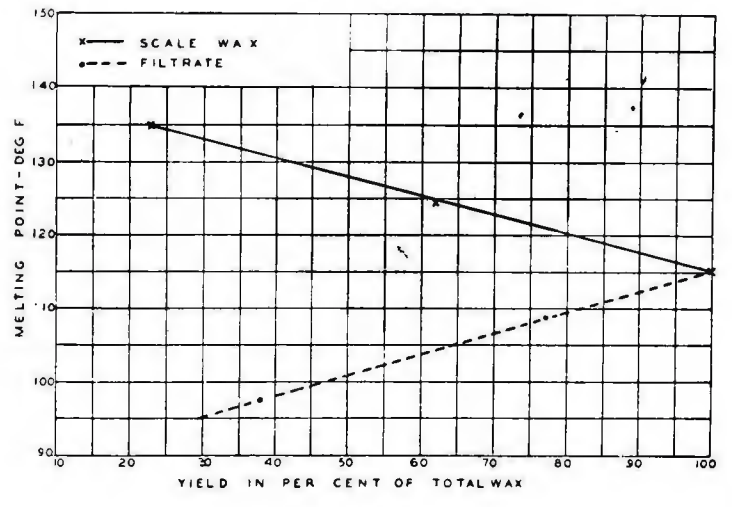


FIGURE 27

Relationship between Melting Point and Yield of Scale Wax

FIG. 27

considerations, either the point R or a point on AC in the region of C must be known. According to Burch[68], the maximum yield of wax of any given melting point obtainable from a given oil-free wax stock may be determined by extraction with solvent (75% acetone + 25% methylene chloride). Burch found that a linear relation exists between the yield and melting point of the solvent free extract and residue, as shown in Fig. 27. Thus, the highest melting wax obtainable from the stock is given by extrapolating to zero yield, and the point R (Fig. 25) could therefore be fixed.

A.H. Etessam[69], working in this Laboratory, has found, however, that the generalisations of Burch apply to a one-stage solvent extraction only, and that by means of multiple stage extractions, waxes (solid phases) of melting point higher than the maximum obtainable in a one-stage extraction, may be obtained.

This method cannot therefore be applied to the determination of point R (and incidentally point C), and moreover, as no satisfactory method appears to be available, it seems that the actual equilibrium diagram cannot be constructed from theoretical considerations used in conjunction with the limited experimental data along the lines indicated.

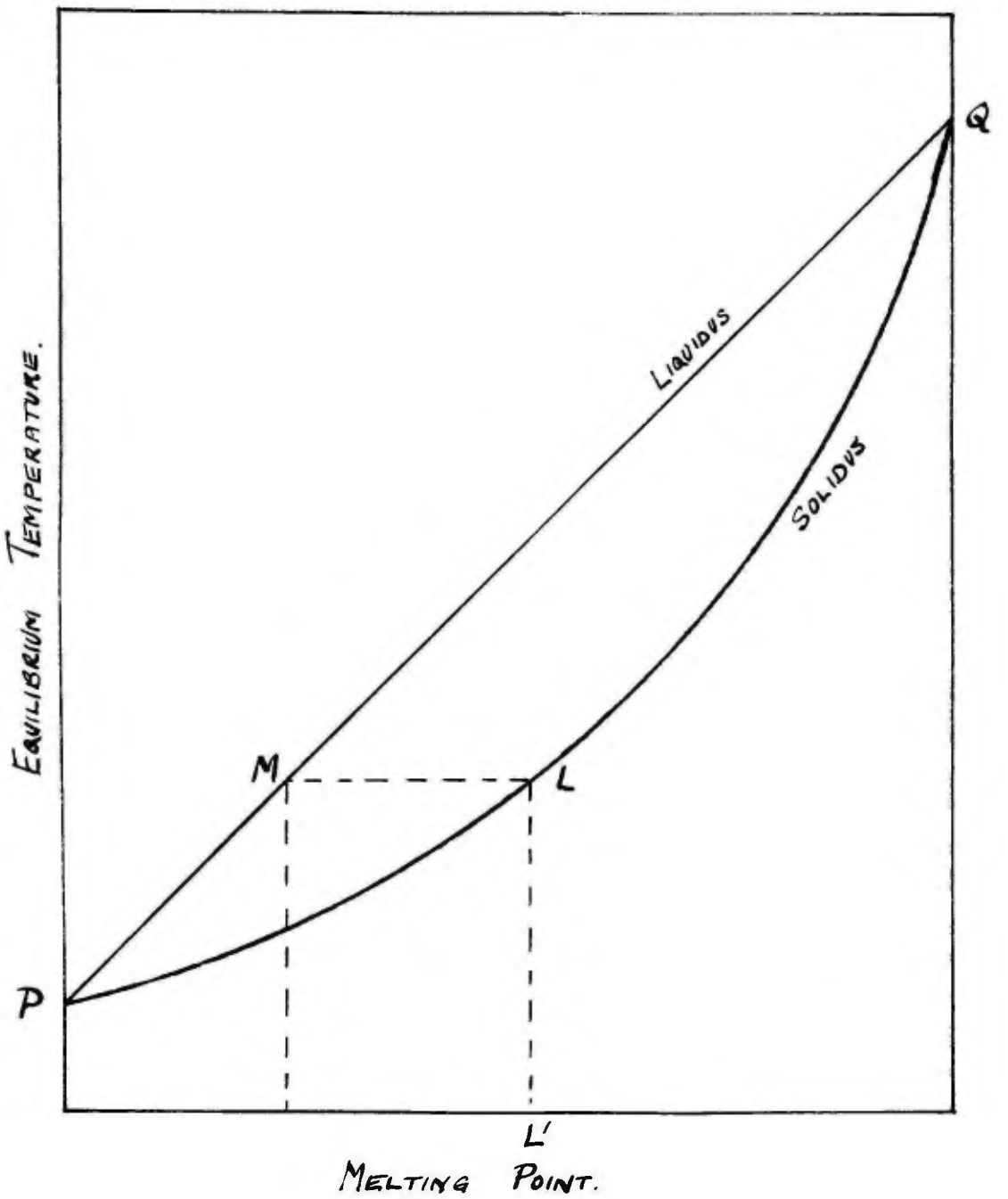


FIG 28(a).

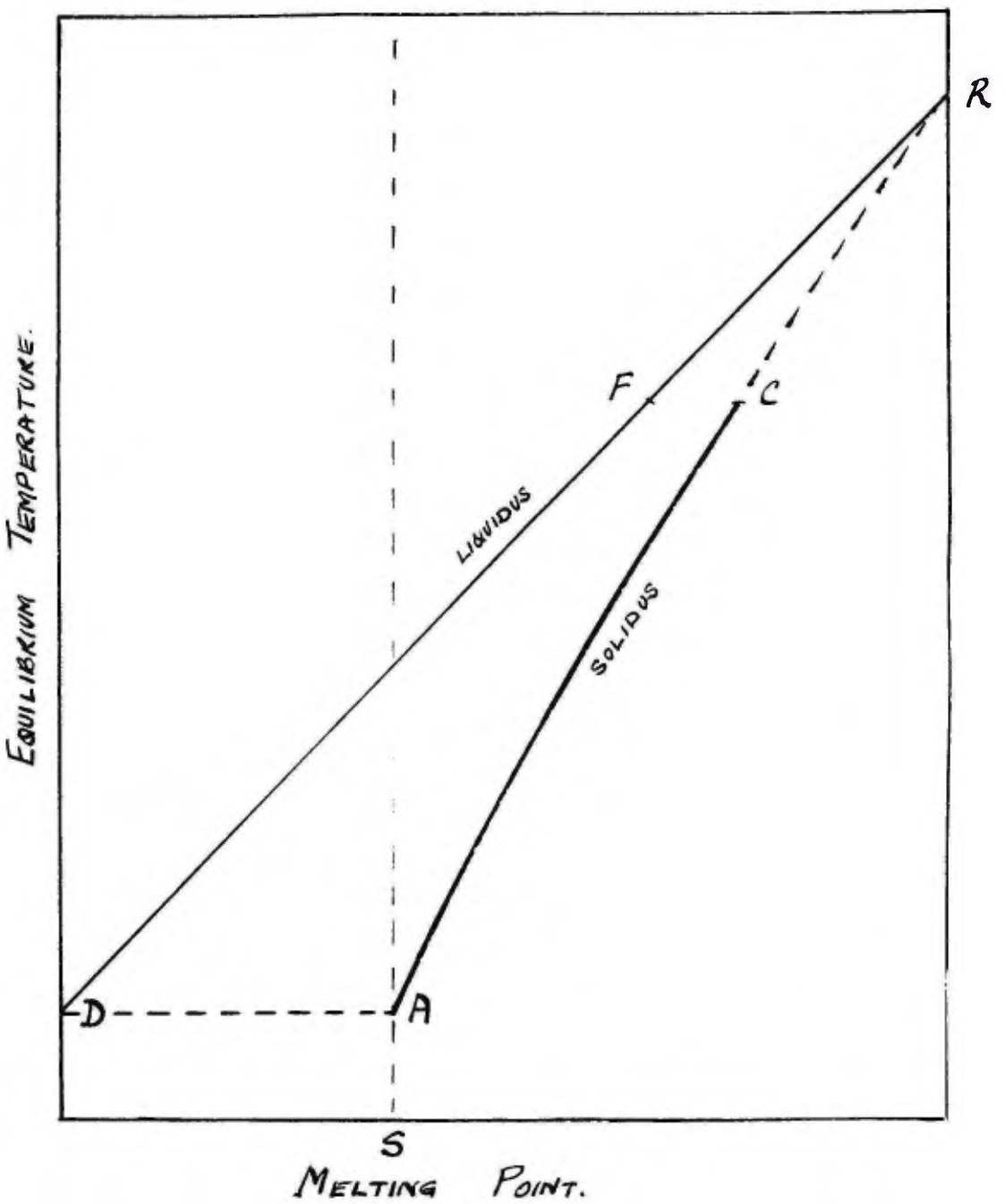


FIG 28(b).

The Wax Equilibrium Diagram - Comparison with Fundamental Equilibrium Diagram representing a Continuous Series of Solid Solutions.

This work was developed from the premise that wax consists of a series of solid solutions, and it is of interest to note that the equilibrium temperature/melting point diagram for two substances forming a continuous series of solid solutions (portion of Fig. 5, Page 20a) shows certain qualitative similarities to the corresponding section of the wax equilibrium diagram (Fig. 25, Page 93a). The essential features of the respective diagrams are reproduced in Figs. 28(a) and 28(b) opposite.

Fig. 28(a) is applicable to any mixture of the two components P and Q, whereas Fig. 28(b) is applicable only to the particular wax stock of melting point S.

In each case, the solidus curves PQ and ACR show the change in composition (melting point) of the solid phases during the ideal process of fractional melting. The liquidus curves PQ and DFR show the composition (melting point) of the infinitesimally small amount of liquid phase in equilibrium with the solid phase at any stage of the process. The liquidus curve PQ is a 45° line, as the melting point of the liquid phase is the same as the equilibrium temperature, whilst the liquidus curve DFR is only slightly removed from a 45° line as the melting point of the liquid phase is, in general, 0.2 - 0.3°F. lower than the equilibrium temperature.

In the case of the pure components P and Q, the solidus and liquidus curves meet at the points representing 100%P and 100%Q as P and Q are pure compounds, and therefore each melts sharply at a definite temperature - the melting point. With the wax mixture, however, the solidus and liquidus curves do not meet at the temperature representing 100% solid phase owing to the melting range of the stock, but at the stage where the yield of solid approaches zero, the two curves tend to meet. This may be explained on the assumption that as the ideal process of fractional melting continues, so the solid phase contains fewer and fewer constituents until in the limit, a pure compound remains.

Finally, consider any mixture of P and Q, (Fig. 28a), indicated by L, which is on the point of melting, and is therefore at its solidification temperature. Under these conditions, the solid L is in equilibrium with the liquid M, and as similar conditions exist at the temperature represented by A and D (Fig. 28(b)), it is clear that section MLQ of Fig. 28(a) is analogous to Fig. 28(b).

The two types of curve therefore show certain similarities.

SECTION III

SECTION 3. - THE SEPARATION OF PARAFFIN WAXES IN PRACTICE.

Introduction.

It has been stated previously that the efficiency of the sweating or fractional melting operation is dependent on some (or all) of the following factors:-

(I) The sweating equipment.

(2) The rate of heating during the process.

(3) The size and shape of the wax crystals, which may be affected by

(a) the composition of the wax.

(b) the amount of oil present in the oil-wax mixture.

(c) the viscosity of the oil,

and (d) the treatment of the wax-oil mixture prior to sweating - the crystal size may be affected by the rate of cooling in the sweater.

It follows that if a single wax stock and the same sweater are employed throughout the investigation, the effects of the following variables must be considered:-

(a) rate of sweating

(b) rate and extent of cooling of the wax or wax-oil mixture in the sweater prior to commencing the sweating operation.

(c) amount of oil in the wax-oil mixture.

(d) viscosity of the oil.

Sweating Methods.

The process may be operated in a number of different ways.

(I) A uniform temperature increase may be employed throughout the sweating period.

(2) A period of gradual temperature rise may be combined with periods of halting or"soaking" at different stages.

(3) The rate of temperature increase may be so regulated that the weight of liquid product collected in a given time remains constant throughout the duration of the experiment.

It is, of course, essential that the sweating experiments should give comparable results, and after considering the above methods in conjunction with the design of the Laboratory sweating apparatus, it was decided that method (3) was the most likely to lead to the accurate control of the operation and therefore give the most satisfactory results.

Sweating Equipment.

Sweating equipment - or the "sweater", as it is more commonly termed - is essentially of three types - pan, tank, and stove. No attempt will be made to give a detailed

description of these different types which are described fairly satisfactorily by their names. In the pan type, the wax is contained in a number of horizontal tanks arranged in tiers; the tank type is essentially a tank filled with tubes and horizontal perforated plates; the sweating stove consists of a cylindrical shell in which are placed a number of cells containing the wax. Tank and stove sweaters are complete in themselves but the pan type is placed in a sweating house or oven which is a vital part of the installation. Many references to commercial plants are given in the literature, but as no description of a Laboratory sweater could be found, it was necessary to design a suitable apparatus.

Satisfactory sweating, besides being dependent on the nature of the wax, is especially sensitive to

(a) the accurate control and regulation of temperature throughout the system, and

(b) an adequate means of draining the liquid formed during the operation.

After due consideration, particularly of these two factors, it was decided that an electrically heated sweater of the stove type would be most likely to fulfil these requirements in Laboratory scale experiments, and a description of the sweater developed for this purpose is given.

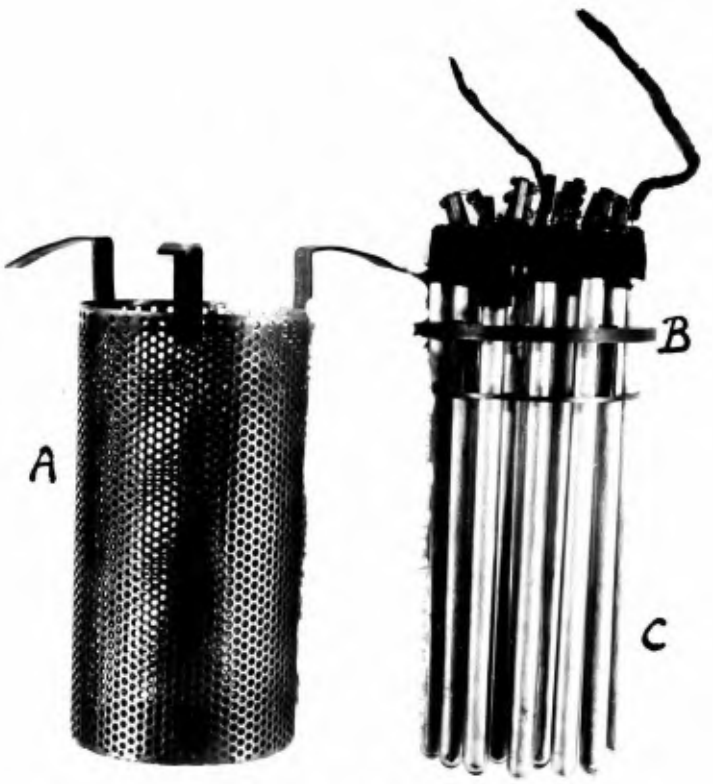


FIG. 29.

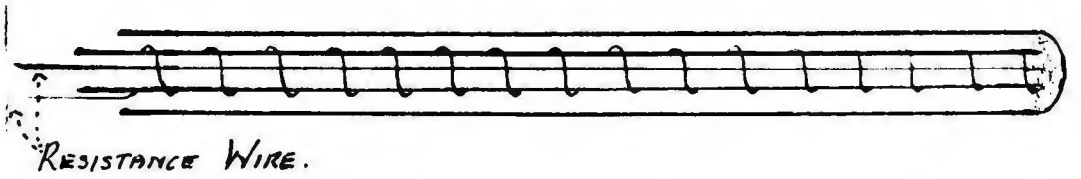


FIG. 30.

Laboratory Sweater.

The sweater consists essentially of a cage in which the wax is supported and which is supplied with a series of internal heating coils, and an external heater in which the cage is enclosed. The component parts are shown in Fig. 29. The cage A is a cylinder of length 6½", diameter 3¼", open at one end and made from perforated brass sheeting having 42 perforations (of diameter 7/64") to the square inch.

The spacer or carrier B, which fits into the open end of the cage, consists of two circular brass discs supported at a distance apart of 1½". Each disc contains 3 small holes for the insertion of thermometers, and 19 holes each of diameter 3/8" arranged symmetrically over the disc. The chief function of the spacer is to maintain the 19 internal heaters C evenly spaced in the cage. This even spacing of the heaters is essential in order to secure a uniform distribution of the heat throughout the wax mass in the sweater.

An internal heater is illustrated in Fig. 30. It consists of an outer glass tube of length 7½" and diameter 5/16", sealed at one end, and which contains the heating element. This consists of 2'6" of resistance wire (resistance 1.08 ohms per foot) supported as indicated on a length of glass tube of considerably smaller diameter.

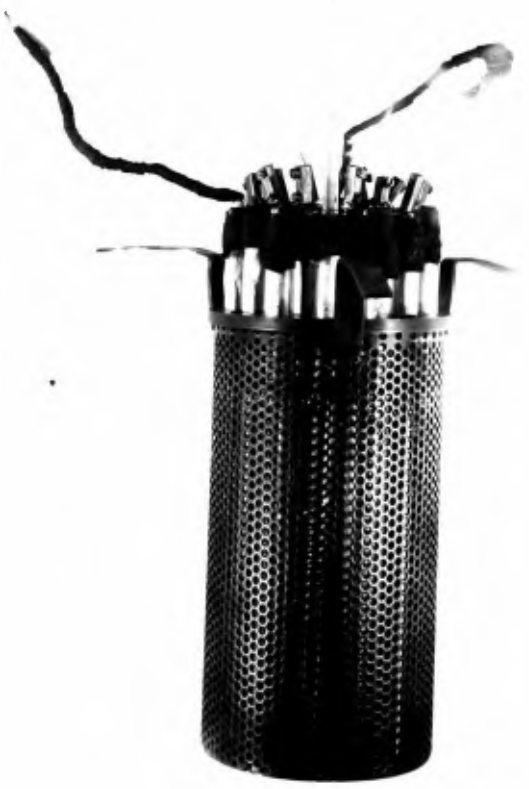


FIG. 31.

A thickness of asbestos paper was placed between the heater and the external glass tube and a small amount of asbestos powder was placed in the bottom of this tube. The asbestos paper and powder were introduced as a precaution against the possible fracture of the glass caused by actual contact with the hot wire. The heating elements were joined in series with small terminal connections.

The internal heating tubes, supported in the spacer, made contact with the bottom of the cage when placed in position in the latter. The set-up of the sweater when ready for experiment is shown in Fig. 31.

The external heater (not shown) consists of an iron sheet welded into the form of a hollow cylinder of length 10½" and diameter 4¾". The outer surface is covered with a layer of asbestos on which is wound the heating element which, in turn, is covered with a thicker layer of asbestos.

Experimental Procedure.

(a) Preparation of Wax Sample.

An initial difficulty was encountered in filling the sweater with the wax sample. Originally, approximately twice the amount of wax required was liquefied in a beaker of slightly larger dimensions than the sweater. The latter was plunged into the molten wax, which was then allowed to solidify completely. After twelve hours, the beaker was momentarily placed in a bath of hot water to release the wax mass from its inner surface. The solid wax was then removed from the surface of the sweater, thus making the latter ready for experiment. It was found, however, that owing to fractional crystallisation in the wax mass, the wax inside the sweater was of higher melting point than the wax outside. The difference - which was as much as I°F - persisted even when the ratio of solid inside : solid outside the sweater was reduced. It was therefore necessary to devise a means of introducing the liquid wax directly into the sweater.

The following method was found to be very satisfactory. The outer surface of the sweater was completely covered with a sheet of cellophane, which was held tightly against the surface by means of a number of rubber bands. Additional support was afforded the cellophane covering the bottom of the sweater by placing the latter in a suitable tin-lid

containing a small amount of molten wax. The wax was caused to solidify by placing the bottom of the apparatus in cold water. In order to heat the glass containing the internal heating elements, current was passed through the latter for a short period, after which the molten wax sample, which had been maintained at a temperature 15-20°F above its melting point, was introduced into the apparatus through a glass filter funnel inserted into one of the thermometer holes in the spacer. The cage was filled to within ½" below the lower plate of the spacer, the capacity being approximately 440 grams of wax. The sweater and its charge were then placed in a fume cupboard away from draughts and allowed to cool under any desired conditions; cooling to room temperature normally occupied between six and seven hours, as indicated by the following figures for a normal cooling:-

Temp. of Mass °F.	Time in Minutes.
145	0
136	5
126	13
122.5	24
122.2	40
122.0	47
121.8	58
119.8	69
114.5	78
82.5	300

FIG. 32.

At the end of this period, the lower portion of the apparatus was momentarily placed in warm water to loosen the wax adhering to the tin. The cellophane covering was then removed from the surface of the sweater and the very thin layer of wax partially covering the latter was removed by scraping with a thin nickel spatula. The sweater was then ready for experiment.

(b) Arrangement of Apparatus.

For the actual sweating or fractional melting experiment, the sweater and external heater were arranged as indicated in Fig. 32 opposite. The external heater was supported in a suitable tripod in which was placed a glass filter funnel of diameter 4" (i.e. of larger diameter than the sweater). A screen of asbestos paper (not shown in photograph) was placed round the tripod. The sweater was supported in the centre of the external heater. During the experiment, drops of liquid fall from the sweater into the filter funnel and thence into a 100 ccs. beaker. It was found, especially during the later stages of the experiment when the liquid phase consisted of waxes of higher melting point, that the liquid tended to solidify in the filter funnel. This was prevented by maintaining a minute gas flame in a position between the beaker and of one of the tripod legs - the hot air from the flame being deflected

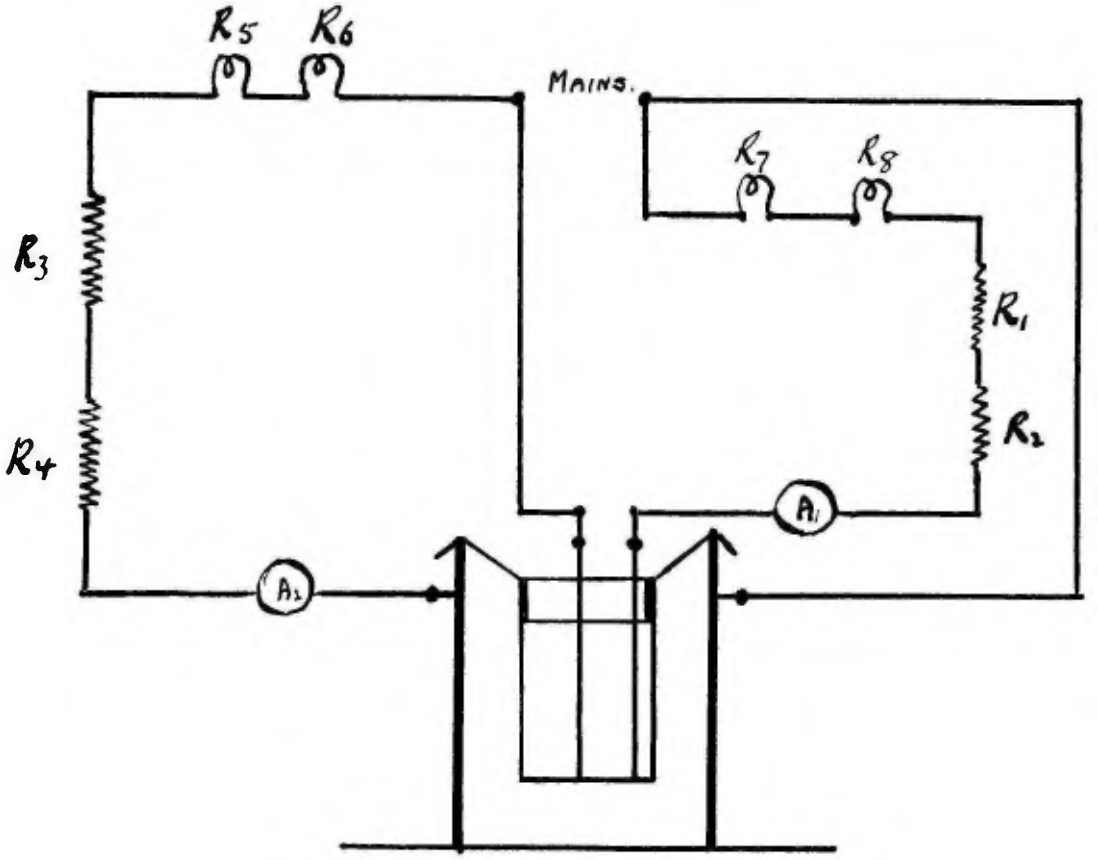


FIG. 33.

on to the filter funnel by means of a small sheet of tin (not shown in diagram) held in a clamp.

(c) Heating Circuit.

The simple electrical heating arrangement is shown in Fig. 33, and is self explanatory. There are two separate circuits.

(a) Internal Heating, comprising variable resistances R_1 and R_2; fixed resistances R_7 and R_8; ammeter A_1 (range 0-250 milliamps); and the internal heating elements of the sweater.

and

(b) External Heating, comprising variable resistances R_3 and R_4; fixed resistances R_5 and R_6; ammeter A_2 (range 0-1 amp); and the external heater.

(d) General.

After experience in regulating the sweater had been gained in some preliminary runs, little difficulty was encountered in maintaining any desired rate of sweating between 3% and 15% per hour, but at rates higher than this upper limit, the experiment tended to become unmanageable. With care and constant attention, it was possible to limit the temperature gradient through the wax mass to 2-3°F for oil-free waxes,

and to 1°F for waxes containing oil.

The external heating was regulated so that the temperature of the air in the space between the sweater and the external heater was within ±0.5°F. of the temperature of the liquid phase dropping from the sweater.

In general, the "sweats", or liquid fractions, were collected in cuts of approximately 5% (by weight). Beakers of 100 ccs capacity numbered from 1 to 25 were kept for this purpose, the simple precaution of numbering eliminating any possible mixing of the samples.

EXPERIMENTAL STUDY OF THE FRACTIONAL MELTING AND SWEATING PROCESSES.

The experimental work will be considered in two sections:-

(A) fractional melting of the oil-free wax stock used in the determination of the equilibrium diagram. For convenience, this process will frequently be referred to as "sweating".

(B) sweating of wax-oil mixtures prepared from this oil-free wax stock and a wax-free oil.

Section (A) - Fractional Melting of Oil-Free Wax.

In the absence of oil, two only of the four variables given on Page *los* have to be considered.

(a) rate of "sweating", and

(b) rate and extent of cooling of the wax prior to "sweating".

The time/cost factor is of great industrial importance, but for various reasons this variable cannot receive consideration here. The object of the sweating process is twofold - (I) to remove oil and (II) to obtain as high a yield as possible of a wax of desired melting point and hence,

in the absence of oil, the latter becomes the principal object.

For the purpose of investigating the effect of the "sweating" rate on the yields of products, a series of experiments (Experimental Runs Nos. 1-8) was made covering the range 3% - 20% per hour. The following comments apply generally to these experiments:-

(I) The wax sample in each case was prepared according to the procedure already described and then allowed to solidify overnight.

(2) The temperatureof the wax mass was gradually increased from room temperature, over a period of 4-4½ hours, before the appearance of the first drops of liquid in the collecting beaker. From this stage the heating was arranged so that the fractional melting proceeded at the desired rate.

(3) The first and, on occasion, the second fraction - representing a 5-I0% yield - were collected at a slightly slower rate, this precaution being taken to avoid the possibility of the experiment getting out of control in the early stages. When I0% had been collected the fractional melting was proceeding at the desired rate.

(4). When less than 5% of the wax remained in the sweater, the current passing through the internal and external heaters was increased considerably in order to facilitate the removal of the wax. The last traces were removed by supporting the sweater (with internal heaters) in an air oven maintained at a temperature of 150-160°F. and allowing the last drops to fall into the collecting beaker. The draining was assisted by occasionally shaking the apparatus, and by following this procedure the amount of wax finally remaining in the sweater was seldom more than one gram.

(5). When the liquid phase was removed at rates of 10% per hour and higher, the experiment was completed in one day, but for rates of 5% and 3% per hour, two and four days respectively were required for the completion of the runs. During the first day of the 5% per hour runs, 50-60% of the wax was removed from the sweater, and that remaining in the apparatus was allowed to cool to room temperature overnight. On the following day, the wax mass was slowly warmed over a period of 4½-5 hours before the first drops of liquid phase were collected.

By careful regulation of the heating it was possible to control the rate to ±0.5% per hour, except in the 20% per hour run, where the rate was too high for accurate control.

(6). A temperature gradient of 2-3°F normally existed in the wax mass during the first half of the run when the larger quantity of wax was present in the sweater. As the experiment progressed however, this temperature gradient became less.

(7). It was found to be very difficult to maintain the desired "sweating" rate during the fractionation of the last 10% owing to the comparatively small amount of wax present in the sweater at this stage. Any errors involved are, however, small and relatively unimportant.

Experimental Runs Nos. 1-8. Results.

The wax used in these experiments was taken from the stock of melting point 122.1°F used for the determination of the equilibrium diagram.

The "sweats" were, in general, collected in cuts of 5% by weight and the melting point of each fraction was determined in the manner previously described.

In order to obtain the figures for a comparison of the relative efficiencies for the different rates of separation of the waxes, it is necessary to know the yield and melting point of the residual wax present in the sweater at any given stage of the experiment. This may be found by:-

(a) Blending the fractions - starting with the last two collected - and determining the melting point of the blend after the addition of each two consecutive fractions, or

(b) Calculation, employing the relationship $T = \frac{414.5\ M}{M + 94.4}$ as previously described (Page 72).

Excellent agreement was found between experimental and calculated figures.

Only the essential figures for each run are given in the following tables of results, and a comparative study of them will be made later. Run No.8 (3% per hour) will receive a

more detailed consideration, as being the slowest run made, it represents the nearest approach to the ideal process.

The following abbreviations are used in the Tables of results:-

Wt. = Weight of fraction in grams.

% = % Yield (by weight).

M.P. = Actual melting point.

M.W. = Hypothetical molecular weight calculated from the relation $T = \frac{414.5M}{94.4+M}$

M.P. (calc) = Melting Point calculated from this relation.

Experimental Run. No. 1.

Remarks:- This experiment was in the nature of a trial, with the object of gaining experience in controlling the rate of heating for this particular wax stock.

A heating period of two hours was allowed before the appearance of the initial drops of liquid phase from the sweater. When "sweating" commenced, there existed a temperature gradient of 6°F between the top and bottom of the wax mass, thus indicating that the initial heating or "warming-up" period was insufficient. In subsequent experiments a considerably longer period was allowed, which resulted in a smaller temperature gradient.

The "sweats" were collected at the rate of 10% per hour and an attempt was made to maintain this rate with a uniform increase in temperature. This method was quite satisfactory until 35% of the wax had been removed, at which point the "sweating" rate increased rapidly and the control of the experiment became very difficult. In the other experiments with this wax stock it was necessary to reduce the rate of heating at this stage of the experiment. It is suggested that the sudden increase in the amount of liquid phase present in the sweater at this stage may be due to the presence in the wax of a relatively large proportion of wax components melting in the range 116-122°F.

The actual results are not included here as they will receive no further consideration.

Experimental Run No. 2. Rate of "Sweating":-15% per hour.

Remarks: Normal process.

Fraction No.	LIQUID PHASE Wt. -	% -	M. P. °	M. W. -	RESIDUAL WAX IN SWEATER. %	M. W.	M. P. (calc)	M. P.
					100.0	333.6	121.9	122.0
1	18.46	5.9	109.05	302.2	94.1	335.5	122.65	-
2	19.03	6.1	111.7	308.4	88.0	337.5	123.4	123.5
3	26.14	8.3	114.05	314.1	79.7	339.9	124.3	-
4	21.92	7.0	114.7	315.5	72.7	342.2	125.2	125.25
5	20.89	6.7	116.7	320.3	66.0	344.5	126.05	-
6	22.23	7.1	118.3	324.3	58.9	346.8	126.9	127.0
7	21.48	6.9	119.85	328.2	52.1	349.3	127.85	-
8	19.48	6.2	120.85	330.7	45.8	351.8	128.8	128.7
9	23.16	7.4	122.3	334.6	38.5	355.1	129.95	-
10	19.71	6.3	123.4	337.5	32.2	358.5	131.15	131.15
11	16.63	5.3	125.8	343.8	26.8	361.5	132.2	-
12	21.50	6.9	127.55	348.5	20.0	265.7	133.7	133.7
13	19.50	6.2	130.75	357.3	13.8	369.6	135.0	-
14	15.52	5.0	131.85	360.3	8.8	375.0	136.8	136.8
15	15.33	4.9	134.95	369.4	3.9	382.0	139.0	139.0
16	12.31	3.9	139.0	382.0	0	-	-	-

Experimental Run No. 3. Rate of "Sweating" I0% per hour.

Remarks:- Normal process.

	LIQUID PHASE				RESIDUAL WAX IN SWEATER.			
Fraction No.	Wt.	%	M. P.	M. W.	%	M. W.	M. P. (calc.)	M. P.
0	-	-	-	-	I00. 0I	333. 8	122. 0	122. 0
1	8. 74	2. 3	I07. 5	299. 0	97. 7	334. 6	122. 25	-
2	11. 20	3. 0	I09. 7	303. 8	94. 7	335. 6	122. 65	122. 6
3	14. 45	3. 0	II0. 95	306. 6	90. 8	326. 8	123. 15	-
4	16. 69	4. 5	112. 5	3I0. 3	86. 3	338. 1	123. 6	123. 5
5	20. 31	5. 4	114. 4	314. 8	80. 9	339. 7	124. 2	-
6	18. 73	5. 0	115. 15	316. 6	75. 9	341. 2	224. 8	124. 75
7	16. 75	4. 5	116. 3	319. 5	71. 4	342. 6	125. 3	-
8	16. 79	4. 5	116. 1	319. 0	66. 9	344. 2	125. 95	125. 9
.9	21. 33	5. 7	117. 7	322. 7	61. 2	346. 2	126. 7	-
I0	22. 35	6. 0	118. 8	325. 4	55. 2	348. 4	127. 5	127. 5
11	21. 29	5. 7	120. 45	329. 9	49. 5	350. 5	128. 3	-
12	15. 99	4. 3	120. 7	330. 5	45. 2	352. 5	129. 05	128. 95
13	22. 22	6. 0	121. 1	331. 4	39. 2	355. 8	130. 2	-
14	23. 31	6. 3	122. 95	236. 3	33. 0	359. 6	131. 55	131. 5
15	19. 62	5. 3	125. 85	344. 0	27. 7	362. 3	132. 5	-
16	19. 00	5. 1	127. 4	348. 1	22. 6	365. 6	133. 65	133. 55
17	18. 57	5. 0	129. 1	352. 7	17. 6	369. 3	134. 9	-
18	22. 21	6. 0	131. 5	359. 4	11. 7	374. 2	136. 5	136. 45
19	15. 57	4. 2	133. 8	365. 9	7. 5	378. 7	138. 0	-
20	[illegible]							139. 55
21	13. 48	3. 6	139. 55	383. 6	0	-	-	-

Experimental Run No. 4. Rate of "Sweating" :- 10% per hour

Remarks:-

In this run an attempt was made to maintain the temperature gradient in the wax mass at less than 1°F by keeping the air surrounding the sweater at a temperature 2°-3°F higher than that of the wax in the upper region of the sweater.

This method was successful in reducing the gradient to 1°F, but as indicated in Fig. 34 (Page 13/a), the yields of the various waxes are considerably lower than those obtained for the same rate of "sweating" in the normal process. It is probable that excessive fractional melting of the wax occurred near the surface of the sweater due to its becoming overheated, with the result that uniform "sweating" of the wax throughout the mass was not obtained.

Experimental Run No. 4. Rate of "Sweating":- 10% per hour.

Fraction No.	LIQUID PHASE Wt.	%	M. P.	M. W.	RESIDUAL WAX IN SWEATER. %	M. W.	M. P. (calcd)	M. P.
0	-	-	-	-	100.0	333.8	122.05	122.15
1	16.50	4.2	108.7	301.5	95.8	335.2	122.5	-
2	17.92	4.5	111.05	307.0	91.3	336.6	123.05	-
3	21.23	5.3	112.65	310.6	86.0	338.2	123.7	123.75
4	20.48	5.2	114.3	314.7	80.8	339.8	124.3	-
5	17.91	4.5	115.7	317.9	76.3	341.0	124.7	-
6	21.22	5.4	116.75	320.5	70.9	342.6	125.3	125.45
7	18.78	4.7	117.65	322.5	66.2	344.0	125.9	-
8	23.48	5.9	118.65	325.1	60.3	345.9	126.65	-
9	22.90	5.8	119.8	328.0	54.5	347.8	127.3	127.35
10	25.23	6.4	121.15	331.5	48.1	349.9	128.1	-
11	25.72	6.5	122.35	334.7	41.7	352.3	129.05	-
12	24.85	6.3	123.5	337.7	35.4	354.9	129.9	129.95
13	27.87	7.0	124.95	341.6	28.4	358.0	131.05	-
14	27.12	6.8	126.6	346.0	21.5	362.0	132.4	-
15	21.39	5.4	128.15	350.1	16.1	365.9	133.8	133.8
16	22.44	5.7	130.65	357.0	10.5	370.7	135.4	-
17	21.21	5.4	133.4	364.9	5.1	376.7	137.35	137.35
18	20.33	5.1	137.35	376.7	0	-	-	-

Experimental Run No. 5. Rate of "Sweating":- 5% per hour

Remarks.

An attempt to maintain the temperature gradient within 1°F was also made in this run, and on this occasion it was between 0.5 - 0.8°F for 70 per cent of the duration of the experiment.

Melting points of the blended fractions were not determined, as it is clear from the figures given on the following page that the yields of the various waxes would be considerably lower than those obtained in the normal process at a "sweating" rate of 5% per hour.

It is probable that the higher temperature of the air surrounding the sweater caused overheating of the wax near the surface as in Run No. 4, with the result that fractional melting of a thin surface layer of wax was taking place throughout the experiment. This fractional melting is, of course, to be distinguished from the main process taking place throughout the mass, and it is likely that its adverse effect on the yields would be more pronounced at slower rates of melting.

The results of Runs 4 and 5 thus indicate the necessity of preventing local overheating, even to the extent of 2° - 3°F.

Experimental Run No. 5. Rate of "Sweating" :- 5% per hour.

Results.

Liquid Phase.

Fraction No.	Wt.	%	M. P.
1	13.78	3.0	II0.2
2	14.82	3.2	111.0
3	11.64	2.5	112.1
4	14.16	3.0	113.2
5	16.42	3.6	114.0
6	17.43	3.8	115.1
7	16.87	3.7	115.65
8	18.13	3.9	116.55
9	13.62	3.0	117.1
I0	16.07	3.5	118.0
11	24.03	5.2	118.7
12	23.50	5.1	119.0
13	15.85	3.4	119.95
14	17.53	3.8	120.4
15	17.50	3.8	121.75
16	21.47	4.7	123.2
17	22.75	4.9	124.3
18	21.02	4.6	125.5
19	21.24	4.6	126.15
20	22.70	4.9	126.8
21	19.14	4.2	127.95
22	19.29	4.2	129.55
23	21.68	4.7	131.1
24	19.34	4.2	130.6
25	21.07	4.6	135.0

Experimental Run. No. 6. Rate of "Sweating" :- 5% per hour.

Remarks :- Normal process.

	LIQUID PHASE				RESIDUAL WAX IN SWEATER.			
Fraction No.	Wt.	%	M. P.	M. W.	%	M. W.	M. P. (calcd.)	M. P.
0	-	-	-	-	100.0	333.4	121.9	121.95
1	13.00	3.2	108.2	300.4	96.8	334.5	122.25	-
2	16.06	4.0	109.0	302.2	92.8	335.9	122.8	-
3	22.21	5.5	111.35	307.6	87.3	337.6	123.4	-
4	24.55	6.1	112.4	310.1	81.3	339.7	124.2	-
5	23.25	6.8	113.45	312.5	74.5	342.2	125.2	125.25
6	22.03	5.4	115.05	316.3	69.0	344.2	125.95	-
7	21.26	5.3	116.65	320.2	63.8	346.2	126.7	-
8	23.32	5.8	118.3	324.4	58.0	348.4	127.5	-
9	23.21	5.7	119.8	328.0	52.3	350.6	128.35	128.35
10	23.25	5.7	120.5	330.0	46.5	353.1	129.25	-
11	16.75	4.1	120.8	330.7	42.4	355.3	130.05	-
12	19.92	4.9	121.8	333.3	37.5	358.3	131.15	131.1
13	25.88	6.4	123.8	338.5	31.1	362.3	132.5	-
14	16.20	4.0	126.25	245.0	27.1	364.9	133.4	-
15	34.74	8.6	128.4	350.7	18.5	371.4	125.6	135.5
16	21.38	5.3	130.65	257.0	13.2	377.3	137.6	-
17	16.06	4.0	133.15	364.1	9.3	382.6	139.25	-
18	17.40	4.3	136.5	374.2	5.0	389.7	141.2	141.2
19	20.21	5.0	141.2	389.7	0	-	-	-

Experimental Run. No. 7. Rate of Sweating:- 20% per hour.

Remarks:- Normal Process.

Fraction No.	LIQUID PHASE Wt.	%	M. P.	M. W.	RESIDUAL WAX IN SWEATER %	M. W.	M. P. (calc)	M. P.
0	-	-	-	-	I00.0	333.6	121.95	122.0
1	18.38	4.0	I09.6	303.6	96.0	334.9	122.4	-
2	22.07	4.8	111.2	307.3	91.3	336.3	122.95	-
3	28.26	6.1	114.6	315.3	85.1	337.9	123.6	-
4	26.38	5.7	115.5	317.5	79.4	339.3	124.05	124.05
5	30.02	6.5	116.5	320.0	73.0	341.0	124.7	-
6	29.82	6.5	117.6	322.6	66.5	342.7	125.4	-
7	34.87	7.5	119.25	326.6	59.0	344.8	126.15	-
8	32.15	7.0	120.45	329.8	52.0	346.8	126.95	-
9	31.49	6.8	120.75	330.6	45.2	349.4	127.9	127.95
I0	29.79	6.4	122.0	333.8	38.8	351.9	128.8	-
11	29.71	6.4	123.15	336.8	32.3	354.8	129.9	-
12	26.78	5.8	124.2	339.7	26.6	358.2	131.1	-
13	23.04	5.0	125.75	343.7	21.6	361.4	132.15	-
14	26.98	5.8	126.7	346.2	15.7	367.0	134.1	134.1
15	29.06	6.3	130.4	356.2	9.5	374.0	136.45	-
16	29.47	6.4	134.5	368.0	3.1	386.4	140.25	140.25
17	14.28	3.1	140.25	386.4	0	-	-	-

Experimental Run. No. 8. Rate of Sweating:- 3% per hour.

Remarks:- Normal process.

	LIQUID PHASE				RESIDUAL WAX IN SWEATER			
Fraction No.	Wt.	%	M. P.	M. W.	%	M. W.	M. P. (Calc)	M. P.
0	-	-	-	-	100.01	333.7	122.0	122.05
1	18.68	4.8	106.25	296.2	95.2	335.6	122.65	-
2	21.92	5.6	109.05	302.3	89.6	337.6	123.45	123.5
3	20.52	5.3	110.0	304.6	84.3	339.8	124.35	-
4	26.78	6.9	112.6	310.5	77.4	342.3	125.2	125.2
5	22.58	5.8	113.75	313.2	71.6	344.6	126.05	-
6	24.91	6.4	116.5	319.9	65.2	347.1	127.05	127.0
7	23.80	6.1	118.35	324.5	59.0	349.4	127.9	-
8	22.94	5.9	119.4	327.0	53.1	351.9	128.85	128.9
9	23.02	5.9	120.2	329.2	47.2	354.8	129.9	-
10	23.16	6.0	121.1	331.5	41.3	358.2	131.1	131.2
11	23.11	5.9	123.35	337.3	35.3	361.7	132.3	-
12	26.28	6.8	125.75	343.7	28.6	365.9	133.8	133.8
13	26.60	6.8	127.05	347.1	21.7	371.8	135.75	-
14	22.92	5.9	130.45	356.5	15.8	377.7	137.7	137.75
15	27.47	7.1	133.65	365.5	8.8	387.5	140.65	-
16	13.08	3.4	137.3	376.5	5.4	394.2	142.7	142.7
17	20.62	5.4	142.7	394.2	0	-	-	-

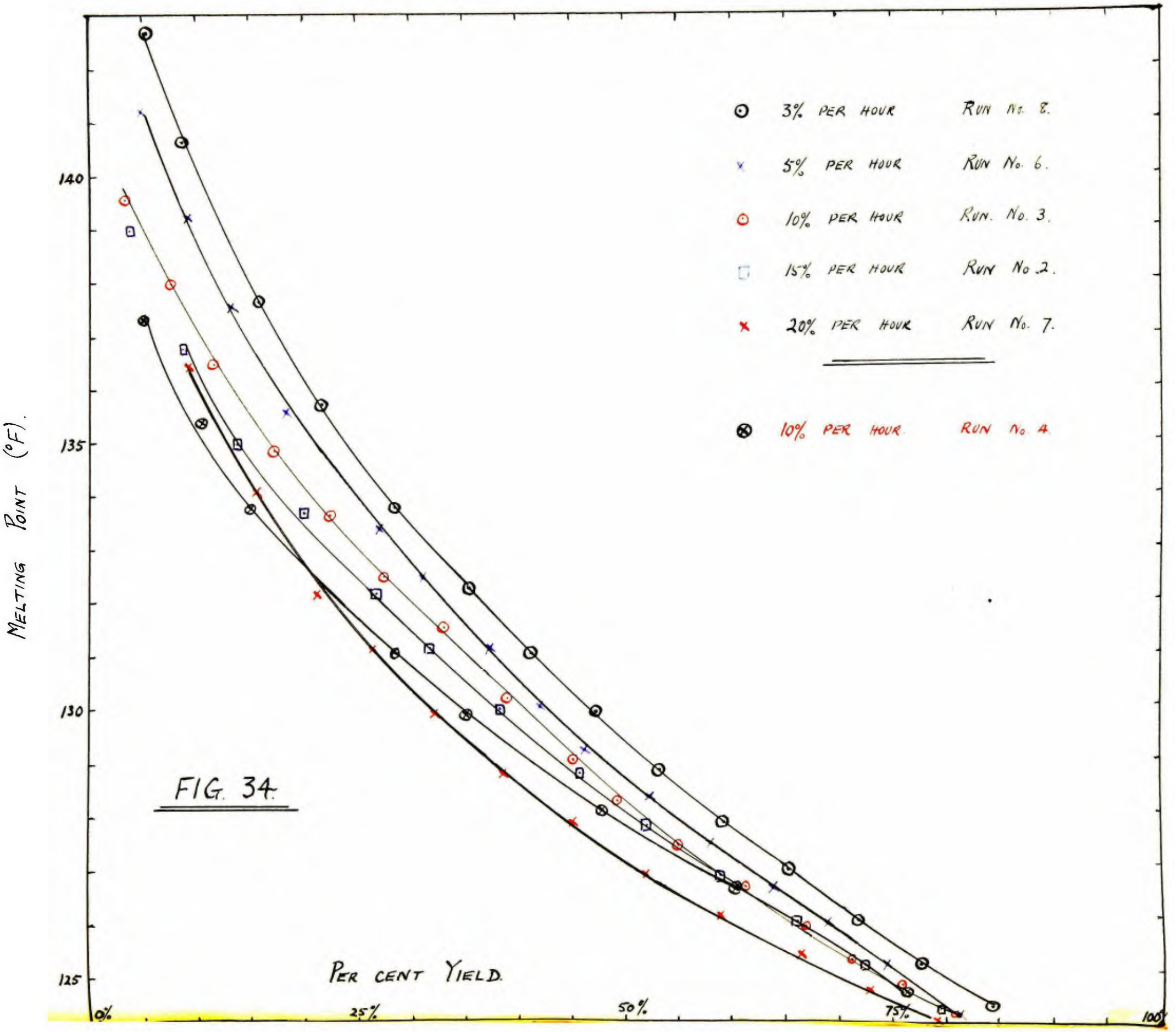

Melting Point (°F).
140
135
130
125
0%
25%
50%
75%
100%
Per cent Yield.
3% per hour Run No. 8.
5% per hour Run No. 6.
10% per hour Run. No. 3.
15% per hour Run No 2.
20% per hour Run No. 7.
10% per hour Run No 4.

FIG. 34.

Experimental Runs 1 - 8. Discussion of Results.

In industry, the process of fractional melting would be continued until the wax remaining in the plant possessed the desired melting point. The yield and corresponding melting point of the wax present in the sweater at any period of the experiment must therefore be considered for each of the different rates of "sweating".

Fig. 34 gives this information for Runs Nos. 8,6,3,2 and 7 conducted at the rates of 3%, 5%, 10%, 15% and 20% per hour respectively. In these particular runs there was one variable only - the rate of "sweating", and the results are therefore comparable. The dotted curve refers to Run No. 4, and as particular mention of this experiment has already been made (Page 24), it will not be considered further.

In Table XXII on the following page, the yields of wax of various melting points are given for each of these runs:-

TABLE XXII.

Melting point. °F.	Yield % (by weight)				
140	10.4	7.4	3.0	-	3.1
137.5	16.5	13.5	8.8	7.0	7.0
135	24.2	21.2	17.2	14.8	13.1
132.5	34.4	31.0	27.5	25.7	20.5
130	47.0	42.9	40.5	38.3	30.8
127.5	61.5	58.0	54.8	55.2	47.5
125	78.8	75.8	74.3	75.0	69.8
Run No.	8	6	3	2	7
"Sweating" Rate (per hour).	3%	5%	10%	15%	20%

For rates of 10% per hour and higher, the yields of wax when less than 10% should be accepted with some reserve as they are probably too high, owing to the difficulty experienced in maintaining the high rate of "sweating" with only a small amount of wax remaining in the sweater.

It is clear from Fig. 34 and from the Table above that the yield of wax of a given melting point decreases with increase in the rate of "sweating".

It is suggested that the relative efficiencies of the

different rates may be obtained most satisfactorily from the yields of 130°F and 132.5°F melting point waxes, for these are present in the sweater in each experiment at a stage when the "sweating" has been proceeding at the desired rate for a considerable period of time. If it is assumed that Run No. 8 (3% per hour) represents a 100% efficient process, then the efficiencies of the other runs, calculated on the basis of the yields of these two waxes, are as given in Table XXIII below:-

TABLE XXIII.

Run No.	Rate of "Sweating" (% per hour)	Efficiency of process calculated from yield of		Mean value.
		130°M.P. wax.	132.5°M.P. wax.	
8	3%	100%	100%	100%
6	5%	91.3%	90.1%	90.7%
3	10%	86.2%	80.0%	83.1%
2	15%	81.5%	74.7%	78.1%
7	20%	65.5%	59.6%	62.5%

In industrial practice, these relative efficiencies would, of course, be considered in relation to the time/cost factor.

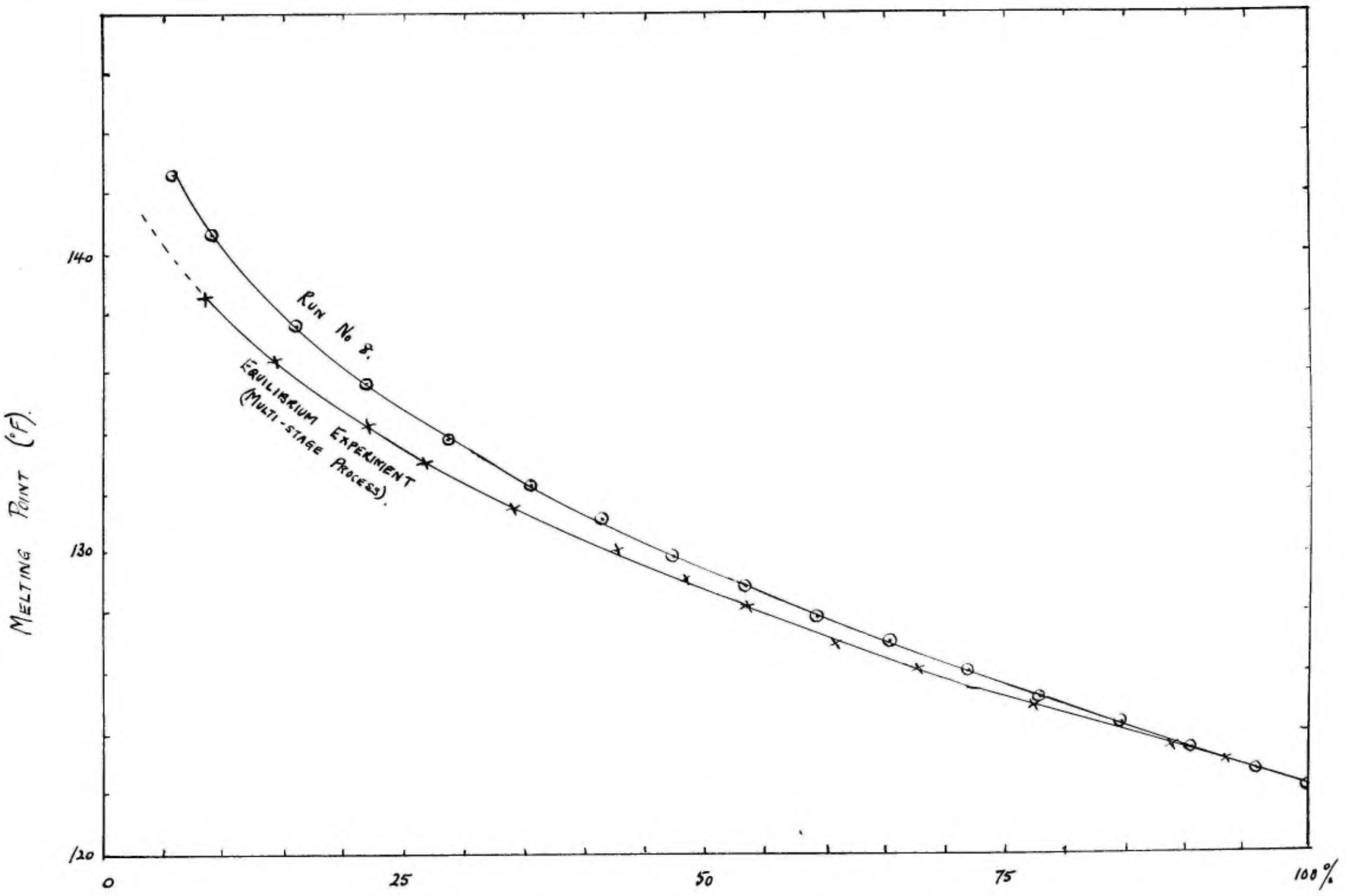

Melting Point (°F).
140
130
120
0
25
50
75
100%
Run No 8.
Equilibrium Experiment
(Multi-stage Process).
Per cent Yield of Solid.

Fig. 35.

Consideration of Run No. 8. (Rate 3% per hour).

This run represents the nearest approach to the ideal or infinite stage process and it will therefore be studied briefly, especially in conjunction with the multi-stage equilibrium experiments (Pages 86 – 92). The following observations are of special interest.

(I) The respective yield/melting point graphs for these two different processes are shown in Fig. 35 opposite, and although the curves are of a similar form, it will be noted that for a given melting point, the yield of wax is higher in the actual "sweating" process than in the multi-stage equilibrium experiment. This finding does not, however, affect in any way the theory developed in connection with the equilibrium diagram, but rather emphasises the experimental difficulties involved in its determination. It is clear that, at least in respect to yields, the actual "sweating" experiment represents a nearer approach to the ideal or infinite stage process than does the equilibrium experiment.

(2). In the multi-stage equilibrium experiments it was found that the melting point of the liquid phase was, in general, 0.2°F lower than the equilibrium temperature. It is therefore of interest to compare the melting points of the individual fractions obtained in Run No. 8 with the temperature at which they left the sweater. The relevant figures are given in Table XXIV on the following page.

TABLE XXIV.

Fraction No.	Melting Point (°F)	Temperature of Wax at end of Cut. (°F)	Difference in Temperature. (°F)
1	106.75	112.7	5.9
2	109.05	114.8	5.7
3	110.0	117.3	6.3
4	112.6	118.0	5.4
5	113.75	118.6	4.8
6	116.5	120	3.5
7	118.35	121.9	3.5
8	119.4	124.2	4.8
9	120.2	124.8	4.6
10	121.1	126.0	4.9
11	123.35	128.0	4.6
12	125.75	129.6	3.8
13	127.05	132.4	5.3
14	130.45	135.0	4.5
15	133.65	139.0	5.4
16	137.3	144.0	6.7
17	142.7	-	-

The difference is considerable, and is undoubtedly connected with the high retentive power of solid wax for liquids. It is suggested that in order to overcome the mutual attraction of the molecules at the surface of the solid wax for the molecules of the liquid wax, an increase in temperature is necessary. The temperature increment causes an increase in the relative amount of liquid phase, and the removal of the latter is then facilitated through the mechanical effect of its own weight.

(3). Although the wax stock is comprised of equal weights of four refined commercial waxes of the following melting points:- 130.95°; 127.85°; 119.85° and I08.35°F, the yield of wax of melting point 130.95°F obtained in Run No. 8 (see Fig.35) is 42%. This high yield indicates that the commercial fractionation of these waxes could have been considerably more efficient.

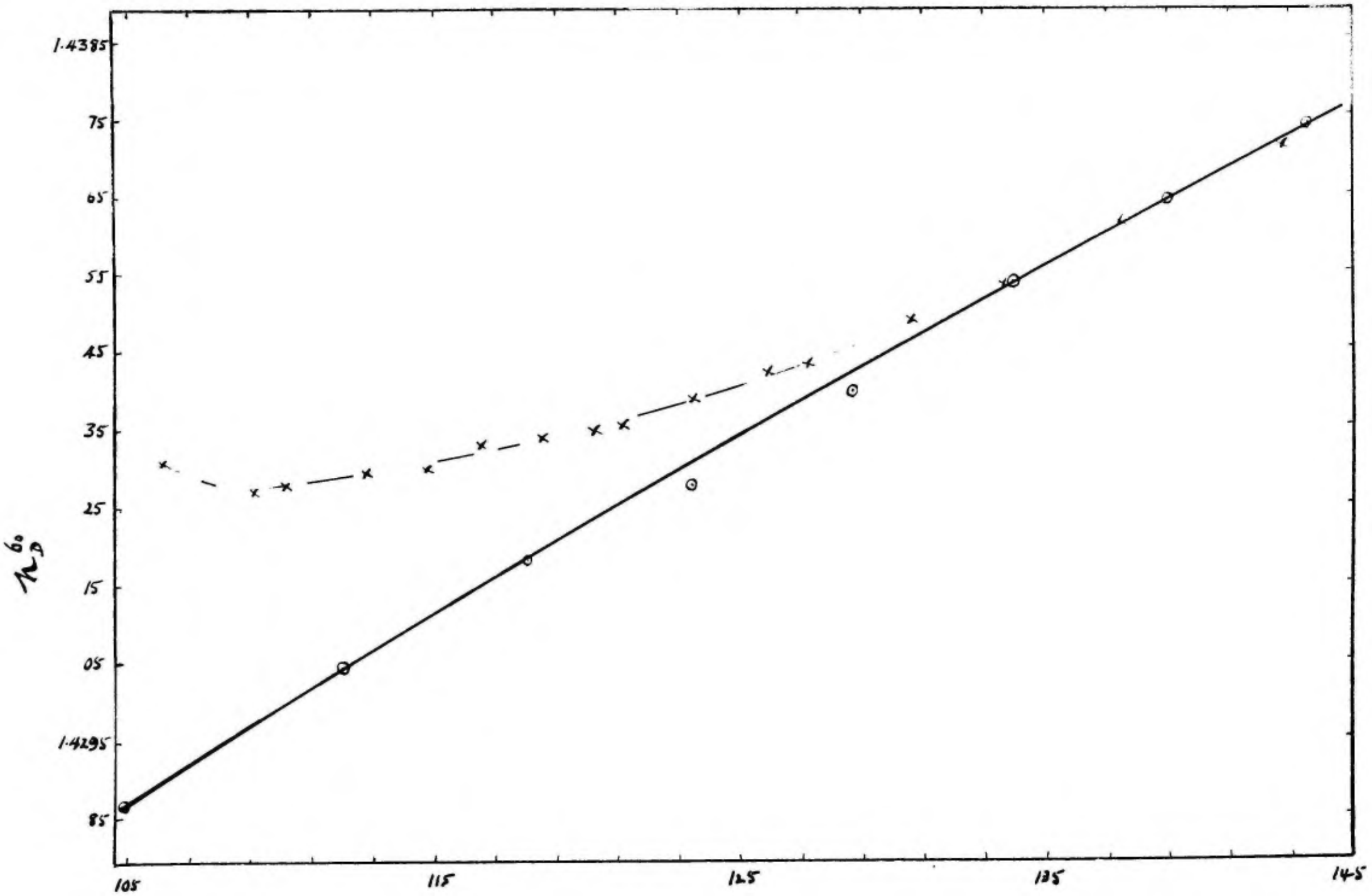

1.4385
75
65
55
45
35
25
15
05
1.4295
85
n_D^{60}
105
115
125
135
145
MELTING POINT (°F).

FIG. 36.

Refractive Index Data - Run No. 8.

The melting point/refractive index (n_d^{60}) relationship for the single fractions collected in Run No. 8 is of special interest when compared with the corresponding relationship for the n-paraffins.

The lower curve in Fig. 36 opposite is plotted from the following values of n_d^{60} for pure n-paraffins taken from various reliable sources.

TABLE XXV.

Carbon atoms in molecule.	Melting Point °C	Melting Point °F.	n_d^{60}
21	40.5	104.9	1.4287
22	44.4	111.9	1.4305
23	47.7	117.9	1.4319
24	51.1	124.0	1.4323
25	53.8	128.8	1.4341
26	56.6	133.9	1.4355
27	59.5	139.1	1.4366
28	62.0	143.6	1.4375

The values of n_d^{60} for each of the wax fractions was determined at 60°C with an Abbé Refractometer. The values for fractions of melting point higher than 60°C were

determined at a temperature 1°C above the melting point, and a correction factor of 0.0004 per 1°C applied to obtain the equivalent value of n_d^{60}. The figures for n_d^{60} given in Table XXVI below are correct to ±0.0001.

TABLE XXVI.

Fraction No.	Melting Point °F	n_d^{60}	Fraction No.	Melting Point °F	n_d^{60}
1	106.25	1.4331	9	120.2	1.4336
2	109.05	1.4327	10	121.1	1.4337
3	110.0	1.4328	11	123.35	1.4339
4	112.6	1.4328/9	12	125.75	1.4342
5	113.75	1.4330	13	127.05	1.4344
6	116.5	1.4332	14	130.45	1.4349
7	118.35	1.4333	15	133.65	1.4354
8	119.4	1.4334/5	16	137.3	1.4362
			17	142.7	1.4373/4

The upper curve in Fig.36 is plotted from the figures given above.

The curve for the wax is initially displaced from the corresponding n-paraffin curve but approaches the latter as the melting point of the fraction increases. The two curves

meet at the point representing Fraction No. 15 and then become almost coincident.

The value of n_d^{60} for the first fraction is higher than n_d^{60} for the second, an anomaly due to the presence in the first fraction of the small amount of oil originally present in the wax stock.

Two possible explanations may be advanced to account for the nature of the curve for the wax fractions:-

(a) The values of n_d^{60} for iso-paraffins are considerably higher than for n-paraffins of the same melting point. It is possible that the wax stock contains iso-paraffins which are gradually removed during the process of fractional melting until removal is complete at Fraction 15, the stage at which the two curves (Fig. 36) meet.

(b) It is more likely, however, that the curve gives an indication of the relative complexities of the fractions, the greater the deviation from the n-paraffin curve the wider is the range of constituents contained in the fraction. Thus, as the fractional melting proceeds, the number of constituents present in the solid phase in the sweater decreases until only a limited number of n-paraffins remain. In the limit, a pure n-paraffin would be obtained. Incidentally, if this explanation is correct, additional support is afforded the interpretation of the wax equilibrium diagram (Page 96).

It should be mentioned, in this connection, that the wax stock of melting point 122.1°F - which almost certainly contains a wider range of constituents than the fraction of the same melting point - has a refractive index of 1.4342, a value slightly higher than that of the single fraction.

Experimental Runs IO and II.

Two runs were made in order to investigate the extent to which the efficiency of the process is dependent on the method of preparing the wax sample prior to "sweating".

Run No. IO. The sweater was prepared in the normal manner and the wax introduced at a temperature of 135°-140°F. The sweater and contents were immediately plunged into a beaker containing acetone cooled with solid CO_2 to -55°C. The acetone was maintained at a temperature of -50 to -55°C during the solid--ification of the wax, which was complete after 35 minutes. After solidification, the wax temperature fell at the rate of 3°F per minute, and when the central region of the mass had cooled to 50°F, the sweater was removed from the acetone bath. The sample remained at room temperature overnight and the "sweating" at the rate of 5% per hour was commenced on the following day.

Some difficulty was experienced in the early stages of the experiment in keeping the temperature gradient of the wax mass within 3°F, but the run proceeded normally after the collection of the first two fractions.

Run No. 11. The sweater was prepared in the normal manner and the wax introduced at a temperature of 135°F. Cooling took place in the absence of draughts until the central region of the wax mass was at a temperature of 110°F. The cellophane was then removed from the outer surface of the sweater and the latter immediately placed inside the external heater which had been heated so that the temperature of the air inside was 105° - 108°F. "Sweating" at the rate of 5% per hour was then conducted in the normal manner, the first drops of liquid appearing in the collecting beaker after one hour's heating.

The "sweating" was very easy to control - much easier than in Runs 1-11-and the temperature gradient in the mass after the collection of the first 5% was 1°F only.

Essential figures for the two experiments are given in the two following pages.

Experimental Run No. IO. Rate of "Sweating" :- 5% per hour.

Remarks:- Normal process after "shock" cooling of sample at -55°C.

	LIQUID PHASE				RESIDUAL WAX IN SWEATER			
Fraction No.	Wt.	%	M.P.	M.W.	%	M.W.	M.P. (calc)	M.P.
0	-	-	-	-	IOO.0	333.4	121.9	122.0
1	21.54	5.3	II0.8	306.4	94.7	334.9	122.45	-
2	21.08	5.2	111.05	306.9	89.5	336.6	123.05	-
3	21.44	5.3	112.65	3I0.7	84.2	338.2	123.7	123.75
4	22.64	5.6	113.75	313.1	78.6	339.9	124.35	-
5	23.26	5.8	115.20	316.7	72.8	341.8	125.05	-
6	25.84	6.4	116.50	319.9	66.4	343.9	125.9	-
7	22.42	5.5	117.60	322.6	60.8	345.7	126.5	126.55
8	25.89	6.4	118.20	324.2	54.4	348.5	127.55	-
9	26.28	6.5	120.15	329.1	47.9	351.1	128.5	-
I0	23.69	5.9	121.15	331.6	42.1	353.8	129.6	-
11	21.73	5.4	122.30	334.7	36.7	356.3	130.4	130.5
12	22.54	5.6	123.25	337.2	31.1	359.9	131.7	-
13	24.89	6.2	124.6	340.6	25.0	360.6	133.3	133.35
14	27.64	6.8	128.5	351.0	18.1	369.8	135.1	-
15	20.91	5.2	130.25	355.8	12.9	375.8	137.1	137.1
16	20.20	5.0	133.45	365.0	7.9	382.3	139.15	-
17	21.00	5.2	137.40	376.9	2.7	392.9	142.15	142.15
18	11.05	2.7	142.15	392.9	0	-	-	-

Experimental Run No. 11. Rate of "Sweating" :- 5% per hour.

Remarks:- Normal process after cooling sample to 110°F.

Fraction No.	LIQUID PHASE Wt.	%	M.P.	M.W.	RESIDUAL WAX IN SWEATER. %	M.W.	M.P. (calc)	M.P.
0	-	-	-	-	100.0	333.6	121.95	122.0
1	18.18	4.4	109.35	303.0	95.6	335.1	122.5	-
2	20.25	4.9	111.05	307.0	90.6	338.6	123.1	-
3	18.69	4.6	112.45	310.2	86.1	338.2	123.7	123.8
4	19.73	4.8	113.95	313.7	81.3	339.7	124.2	-
5	19.66	4.8	114.95	316.1	76.5	341.2	124.8	124.75
6	21.97	5.4	115.7	317.3	71.1	344.4	125.45	-
7	17.45	4.3	116.25	319.3	66.8	347.0	126.0	126.1
8	19.27	4.7	116.85	320.9	62.1	346.1	126.65	-
9	19.37	4.7	117.85	323.1	57.4	348.1	127.4	-
10	18.00	4.4	118.7	325.2	53.0	349.2	128.05	128.15
11	21.04	5.1	119.95	328.5	47.9	352.0	128.9	-
12	20.60	5.0	121.1	331.5	42.9	354.6	129.8	129.85
13	31.66	7.7	122.8	335.9	35.2	358.6	131.25	-
14	19.05	4.6	124.95	341.7	30.5	361.4	132.15	132.2
15	20.74	5.1	126.4	345.4	25.4	364.1	133.2	-
16	21.57	5.3	128.05	349.8	20.2	368.2	134.55	134.55
17	19.90	4.9	129.6	353.9	15.3	371.5	135.7	-
18	18.45	4.5	131.6	359.6	10.8	377.9	137.8	137.85
19	18.62	4.5	134.6	368.2	6.3	386.4	140.25	-
20	17.30	4.2	138.5	380.2	2.1	396.6	143.45	143.45
21	8.45	2.1	143.45	396.6	0			

Experimental Runs IO and II. Discussion of Results.

The melting point/yield graphs (not shown) for Runs IO and 11 are similar in form to those given by the results of the previous runs. The yields obtained in the two experiments under consideration are compared in Table XXVII with those obtained in Run No. 6, which was also conducted at the rate of 5% per hour, but after normal cooling of the sample to room temperature prior to commencing the experiment.

TABLE XXVII

	Yield % (by weight)			
Melting Point (°F)	Normal Cooling.	Partial Cooling.	"Shock" Cooling.	
140	7.4	6.8	6.2	
137.5	13.5	12.0	12.0	
135	21.2	18.8	18.0	
132.5	31.0	28.7	27.6	
130	42.9	41.7	39.2	
127.5	58.0	57.4	54.0	
125	75.8	75.0	73.2	
Run No.	6	11	IO	
Rate	5%	5%	5%	

The differences in the yields from Runs 6 and 11 are small, and it seems that only a slight advantage is to be gained by cooling to room temperature before commencing to "sweat". It is likely that this slight increase in yield would be more than balanced in the industrial process by the increased cost involved in the additional cooling and heating required.

The difficulty experienced in the early stages of Run No. IO in reducing the temperature gradient in the wax mass to the normal figure, is reflected in the lower yields of the lower melting point waxes. It is possible that the "shock" cooling promotes the formation of very small crystals, especially in the region of the surface of the wax, and that these are not conducive to easy "sweating", especially in the early stages of the experiment.

Experiments on the Fractional Melting of Oil-free Wax - General Summary.

The principal deductions from the results of Experimental Runs Nos. 1-11 concerning the fractional melting process for the separation of waxes of different melting points from an oil-free wax stock, may be summarised as follows:-

(I) The rate of melting is the most important variable. As might have been anticipated, the efficiency of the process decreases with increase in the rate at which the process is conducted.

(2) Preparation of the sample by "shock" cooling to room temperature results in a wax mass which is considerably more difficult to "sweat" during the early stages of the process.

(3) Cooling the sample to a temperature slightly below the complete solidification point of the wax before commencing the melting process, results in a mass which is considerably easier to control during the early stages of this latter process. As the yields of the products are only very slightly lower than those obtained by the method involving the cooling of the sample to room temperature, it may be concluded that the more extensive cooling is uneconomical and therefore unnecessary.

(4) Local overheating during the process, even to the extent of 2° - 3°F, has an adverse effect on the yields of the various waxes.

SECTION (B) - SWEATING OF WAX-OIL MIXTURES.

It has been indicated previously that an investigation of the factors affecting the efficiency of the sweating process in which the same oil and wax stocks, and also the same sweater are used throughout, resolves itself into a consideration of the effects of the following variables:-

(1) The amount of the oil in the oil-wax mixture.

(2) The rate of sweating.

and(3) The rate and extent of the cooling of the oil-wax mixture before commencing to sweat.

The effect of (4) viscosity, will be discussed later.

It is believed that no account of such experiments in which synthetic oil-wax mixtures have been used, has so far appeared in the technical literature. Wax distillates of varying oil content obtained directly from the crude by distillation might be employed, and an objection might be raised to the use of synthetic mixtures on the grounds that they are not obtained directly from the crude in the relative amounts in which they are blended. The composition of the stock is, however, immaterial, as it is possible that such a stock could be obtained from a crude. Moreover, there are certain definite advantages attending the use of synthetic oil-wax mixtures:-

(I) Complications due to the variation in composition of the waxes and oils present in the mixture, such as might be encountered when using distillates of different boiling ranges, are eliminated.

(2) there is no longer the necessity for the determination of the oil content of the stock - a difficult experiment, as there is no satisfactory method for the estimation.

(3) the possible yields of the various melting point waxes that may be obtained from the wax stock are already known from the previous fractional melting experiments.

(4) blends of any desired oil content may be prepared very easily.

Oil Stock.

The stock of de-waxed oil which was, of course, essential for this series of experiments, was prepared in the following manner. Dewaxed Second Cooled Blue Oil from the Llandarcy Refinery of the A. I. O. C.* was used as the starting material for the preparation. This oil had been removed from the wax distillate cut by filter pressing at a temperature of 13°F during the normal refinery processing of the distillate. The commercial dewaxed Second Cooled Blue Oil was further dewaxed in the Laboratory with ethylene dichloride at -30°C, using a leaf-filter type dewaxing

* Anglo-Iranian Oil Company.

apparatus devised and successfully applied in the Research Laboratories of the A. I. O. C.

The oil-solvent mixture containing one volume of oil to two volumes of solvent was cooled to -30°C, using solid CO_2, and then filtered from the wax deposited at this temperature. The solvent was removed from the oil by distillation under reduced pressure with a continuous stream of nitrogen being passed through the liquid. The wax-free oil had the following properties:-

Specific Gravity at 60°F = 0.8960.

Refractive Index at 60°F = 1.4867.

Cloud Point = Below -20°C.

Viscosity: Redwood I at 100°F = 64.1 secs.

Redwood I at 140°F = 46.7 secs.

Wax Stock.

The wax stock was that of melting point 122.1°F used in the experiments on fractional melting.

(I) Effect of Oil Content. Experimental Runs 12-16 (incl) and 20.

Experimental Procedure - General Comments.

The following remarks apply generally to the experiments with wax-oil mixtures.

(I) The desired amounts of wax and oil were weighed into a beaker. The mixture was then liquefied, thoroughly stirred, and the sample prepared in the sweater as described for the oil-free wax experiments.

(2) A sweating rate of 5% per hour was employed. This rate, besides being likely to lead to satisfactory results, was also quite convenient as it enabled a run to be completed in two days.

(3) The temperature of the sample in the sweater was gradually increased from room temperature, the time elapsing before the collection of the first drops of liquid phase being dependent on the amount of oil in the sample. This is illustrated in Table XXVIII below:-

TABLE XXVIII.

Oil content of Sample.	First drops of Liquid Phase after	Temperature of mass.
2%	210 mins.	101 °F
5%	180 "	81 °F
30%	30 "	69 °F
40%	10 "	65 °F

From the stage at which the first drops of liquid appeared, the heating was adjusted so that the sweating proceeded at the desired rate. For the wax-oil mixtures of higher oil content, only slight heating was required to maintain the rate during the collection of the first 10%, and during this period it was occasionally found necessary to cut off the current for intervals of a few minutes.

(4) The last 5% (or less) was removed from the sweater as in the experiments with oil-free wax. Difficulty was also experienced in this series of experiments in maintaining the desired rate of sweating during the fractionation of the last 10%.

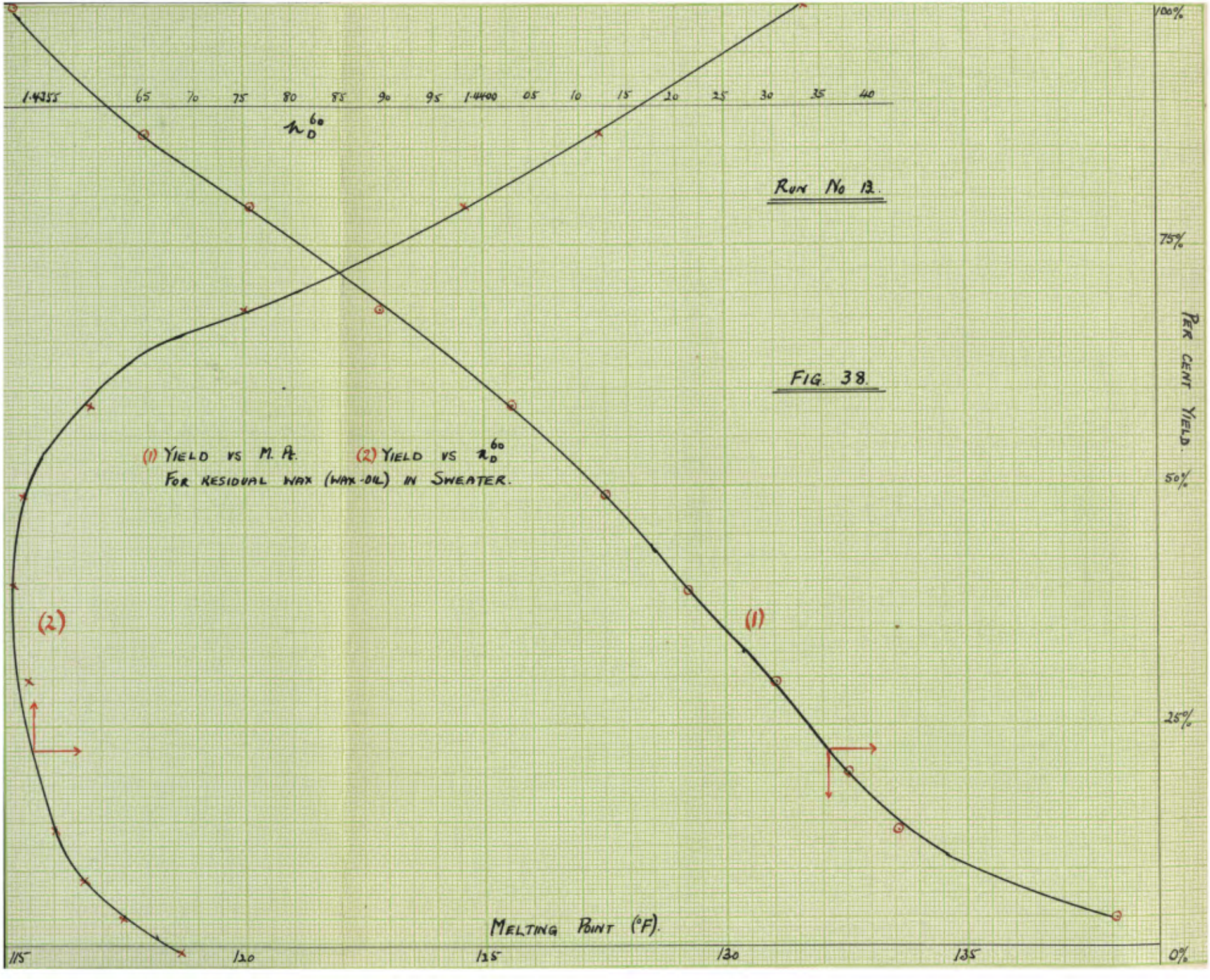
Experimental Runs 12-16 (incl) and 20. Results.

The "sweats" were collected, in general, in cuts of 5% by weight, and the melting point of each fraction of melting point higher than 100°F was determined in the manner previously described. The melting points of fractions lower than 100°F were not determined accurately as the melting point method developed for this work, like the I.P.T. and A.S.T.M. methods, is not satisfactory for mixtures of oil and wax containing large amounts (greater than 50%) of oil. A rough determination was made in some instances, but a knowledge of these low melting points is not essential in this investigation. The refractive index at 60°C was also found for each fraction, using an Abbé Refractometer.

In this series of experiments, as in those with oil-free wax, it is necessary to know the melting point and yield of wax, or oil-wax mixture, present in the sweater at any stage of the experiment. The fractions were therefore blended as before - starting with the last two collected - and the melting point, and also the refractive index at 60°C, found after the addition of each two consecutive fractions.
Owing to the presence of oil, the relationship $T = \frac{414.5XM}{94.5 + M}$ cannot be applied to the calculation of melting points, except for those fractions collected after the removal of all the oil.

It will be noted from the Tables of Results given later that in a few instances the melting point of a fraction is slightly lower than that of the next higher fraction. The fractions concerned are, in each case, the last collected on the first day and the first collected on the second day of a run. The small discrepancies are unimportant. The fractions collected during the first day are those given above the dotted line (see Tables of Results).

The essential figures for each run are given in the following pages, the abbreviations in the Tables being used as before. The graphs given in each instance facing the results show (I) the yield versus melting point, and (2) the yield versus n_d^{60}, for solid phase of melting point higher than 115°F.


1.4355
65
70
75
80
85
90
95
1.4400
05
10
15
20
25
30
35
40
n_D^{60}
RUN NO 13.
FIG. 38.
(1) YIELD VS M. PT. (2) YIELD VS n_D^{60}
FOR RESIDUAL WAX (WAX-OIL) IN SWEATER.
(2)
(1)
100%
75%
50%
25%
0%
PER CENT YIELD.
MELTING POINT (°F).
115
120
125
130
135

Experimental Run. No. 13.

Properties of the Oil-Wax Mixture.

Oil Content = 20%. M. P. = 115.1°F. n_d^{60} = 1.4434.

Remarks. Normal process at 5% per hour.

	LIQUID PHASE (SWEATED FRACTIONS)				RESIDUAL WAX (WAX-OIL) IN SWEATER.		
Fraction No.	Wt.	%	M. P.	n_d^{60}	%	M. P.	n_d^{60}
0	-	-	-	-	100.0	115.2	1.4433
1	58.48	13.1	87.9	1.4575/4	87.0	117.95	1.4412
2	34.15	7.6	93.3	1.4556	79.3	120.1	1.4398
3	24.05	5.4	98.7	1.4547	74.0	-	-
4	23.74	5.3	95.8	1.4531	68.7	122.75	1.4375
5	21.78	4.9	99.15	1.4508	63.8	-	-
6	23.06	5.2	106.3	1.4452	58.6	125.55	1.4359
7	21.57	4.8	113.95	1.4393	53.8	-	-
8	20.44	4.6	114.1	1.4385	49.3	127.5	1.4352
9	21.91	4.9	118.9	1.4357	44.4	-	-
10	22.31	5.0	121.25	1.4353	39.4	129.2	1.4351
11	21.66	4.8	123.4	1.4350	34.6	-	-
12	20.85	4.7	124.35	1.4350	29.9	131.0	1.4352/3
13	24.48	5.5	125.7	1.4350	24.4	-	-
14	22.56	5.0	127.0	1.4350	19.4	-	-
15	21.85	4.9	129.15	1.4351	14.5	133.55	1.4355
16	23.51	5.3	131.15	1.4349	9.2	-	1.4358
17	17.42	3.9	132.55	1.4352	5.4	138.1	1.4362
18	16.71	3.7	136.95	1.4360	1.6	140.85	1.4268
19	7.29	1.6	140.85	1.4368	0	-	-

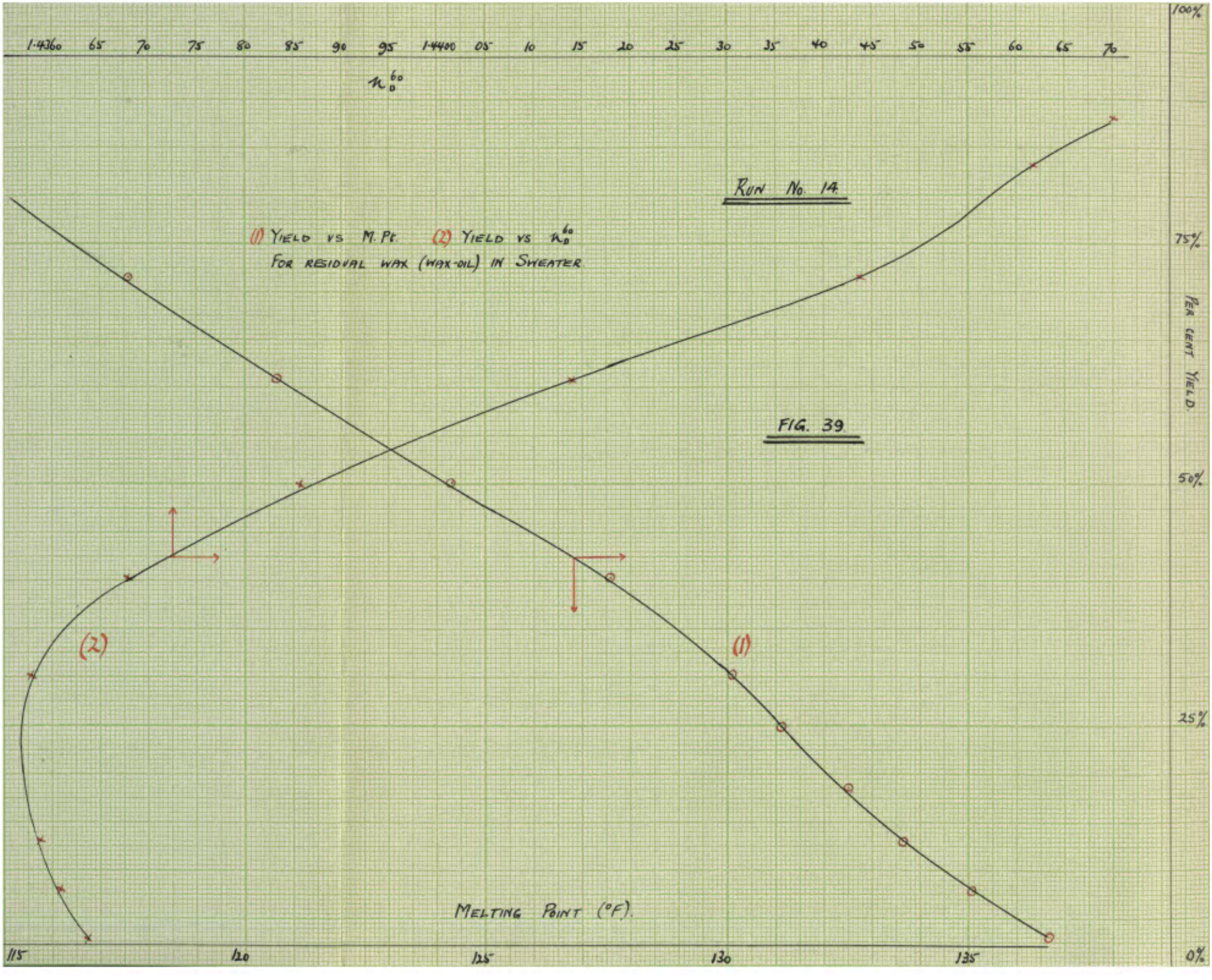
Experimental Run. No. 13.

Properties of the Oil-Wax Mixture.

Oil Content = 20%. M. P. = 115.1°F n_d^{60} = 1.4434.

Remarks. Normal process at 5% per hour.

	LIQUID PHASE (SWEATED FRACTIONS)				RESIDUAL WAX (WAX-OIL) IN SWEATER.		
Fraction No.	Wt.	%	M. P.	n_d^{60}	%	M. P.	n_d^{60}
0	-	-	-	-	100.0	115.2	1.4433
1	58.48	13.1	87.9	1.4575/4	87.0	117.95	1.4412
2	34.15	7.6	92.3	1.4556	79.3	120.1	1.4398
3	24.05	5.4	92.7	1.4547	74.0	-	-
4	23.74	5.3	95.8	1.4531	68.7	122.75	1.4375
5	21.78	4.9	99.15	1.4508	63.8	-	-
6	23.06	5.2	106.3	1.4452	58.6	125.55	1.4359
7	21.57	4.8	113.95	1.4393	53.8	-	-
8	20.44	4.6	114.1	1.4385	49.3	127.5	1.4352
9	21.91	4.9	118.9	1.4357	44.4	-	-
10	22.31	5.0	121.25	1.4353	39.4	129.2	1.4351
11	21.66	4.8	123.4	1.4350	34.6	-	-
12	20.85	4.7	124.35	1.4350	29.9	131.0	1.4352/3
13	24.48	5.5	125.7	1.4350	24.4	-	-
14	22.56	5.0	127.0	1.4350	19.4	-	-
15	21.85	4.9	129.15	1.4351	14.5	133.55	1.4355
16	23.51	5.3	131.15	1.4349	9.3	-	1.4358
17	17.42	3.9	132.55	1.4352	5.4	138.1	1.4362
18	16.71	3.7	136.95	1.4360	1.6	140.85	1.4268
19	7.29	1.6	140.85	1.4368	0	-	-


1·4360 65 70 75 80 85 90 95 1·4400 05 10 15 20 25 30 35 40 45 50 55 60 65 70
n_D^{60}
RUN No. 14.
(1) YIELD VS M. Pt. (2) YIELD VS n_D^{60}
FOR RESIDUAL WAX (WAX-OIL) IN SWEATER.
FIG. 39
(2)
(1)
MELTING POINT (°F).
115 120 125 130 135
100%
75%
50%
25%
0%
PER CENT YIELD.

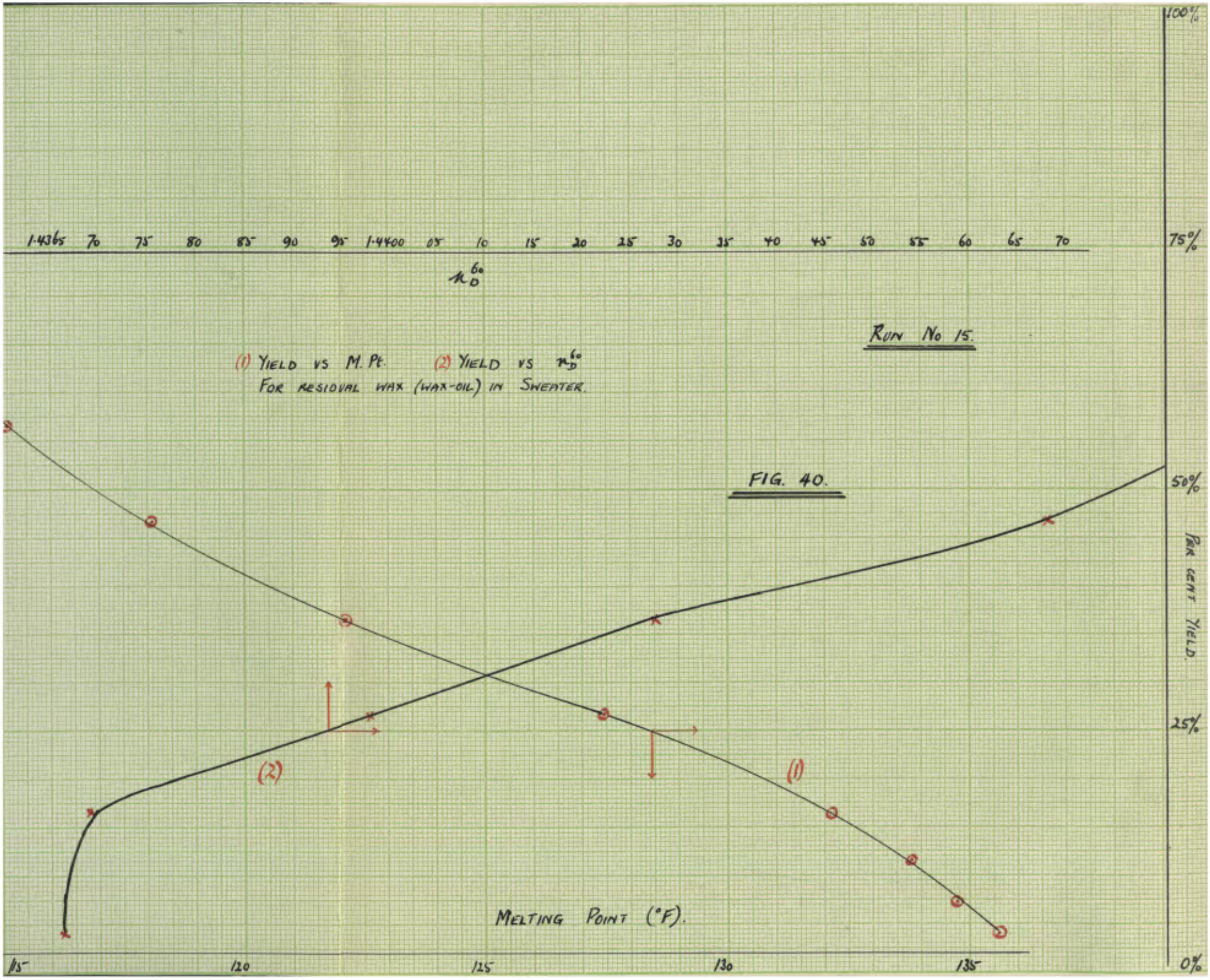
Experimental Run No. 14.

Properties of the Oil/Wax Mixture.

Oil Content = 30%. M.P. = 111.05°F. n_d^{60} = 1.4486

Remarks. Normal process at 5% per hour.

LIQUID PHASE (SWEATED FRACTIONS)					RESIDUAL WAX (WAX-OIL) IN SWEATER		
Fraction No.	Wt.	%	M.P.	n_d^{60}	%	M.P.	n_d^{60}
0	-	-	-	-	100.0	111.05	1.4484
1	48.33	11.2	83 *	1.4627/6	88.8	113.15	1.4470
2	23.43	5.4	87 *	1.4603	83.4	114.15	1.4462/1
3	24.24	5.6	92 *	1.4586/7	77.8	-	-
4	26.72	6.2	92 *	1.4579	71.6	117.6	1.4444
5	24.96	5.8	-	1.4575	65.8	-	-
6	21.92	5.1	-	1.4571	60.7	120.7	1.4414
7	21.79	5.1	-	1.4565	55.7	-	-
8	24.19	5.6	98.8	1.4542	50.1	124.3	1.4386/7
9	21.31	4.9	104.7	1.4496	45.2	-	-
10	20.42	4.7	111.65	1.4447	40.4	127.6	1.4368/7
11	21.48	5.0	118.4	1.4397	35.5	-	-
12	22.67	5.3	120.9	1.4382	30.2	130.1	1.4358
13	22.70	5.3	125.1	1.4362/1	24.9	-	-
14	27.05	6.3	127.15	1.4358/9	18.7	-	-
15	24.67	5.7	129.6	1.4358	13.0	133.7	1.4358
16	21.50	5.0	131.65	1.4356	8.0	-	-
17	22.62	5.2	134.1	1.4357	2.7	136.75	1.4360
18	11.81	2.7	136.75	1.4360	0	-	-


1·4365 70 75 80 85 90 95 1·4400 05 10 15 20 25 30 35 40 45 50 55 60 65 70
n_D^{60}
100%
75%
50%
25%
0%
PER CENT YIELD.
RUN No 15.
(1) YIELD VS M. Pt. (2) YIELD VS n_D^{60}
FOR RESIDUAL WAX (WAX-OIL) IN SWEATER.
FIG. 40.
(2)
(1)
MELTING POINT (°F).
115 120 125 130 135

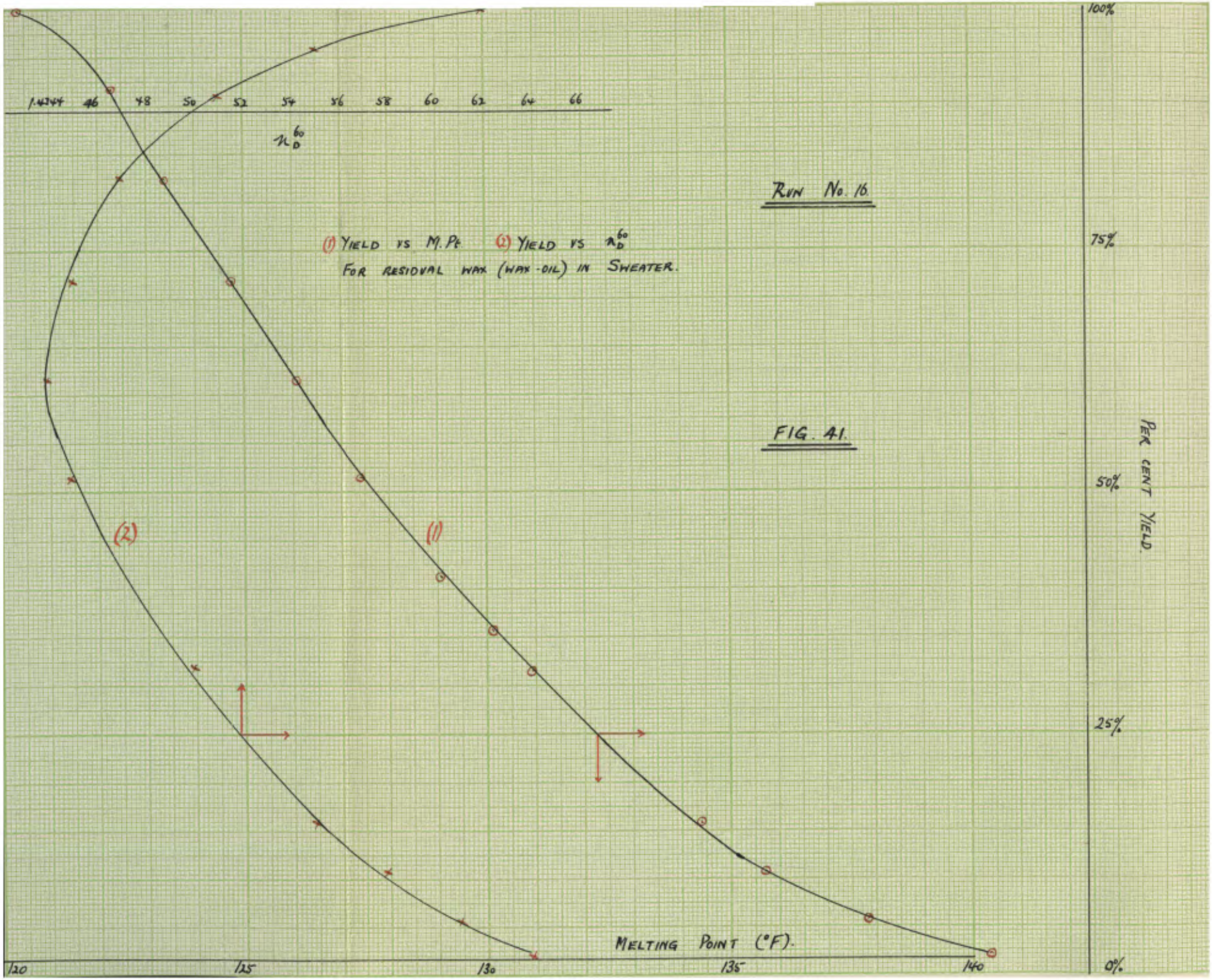
Experimental Run No. 15.

Properties of the Oil/Wax Mixture.

Oil Content = 40%. M. P. = 107.05°F. n_d^{60} = 1.4536.

Remarks. Normal process at 5% per hour.

	LIQUID PHASE (SWEATED FRACTIONS)				RESIDUAL WAX (WAX-OIL) IN SWEATER		
Fraction No.	Wt.	%	M. P.	n_d^{60}	%	M. P.	n_d^{60}
0	-	-	-	-	100.0	107.1	1.4538
1	41.49	9.2	87 *	1.4633	90.8	108.15	1.4528
2	46.47	10.3	91 *	1.4606	80.5	-	1.4520
3	21.84	4.9	92 *	1.4606	75.7	110.8	1.4516/5
4	20.63	4.6	93.5*	1.4601	71.1	-	-
5	20.62	4.6	93.5*	1.4594	66.5	112.8	1.4504
6	21.69	4.8	94 *	1.4592/3	61.7	-	-
7	22.59	5.0	-	1.4588/7	56.7	115.05	1.4486/7
8	21.49	4.8	-	1.4585	51.9	-	-
9	22.94	5.1	-	1.4580	46.8	118.05	1.4468
10	22.69	5.0	-	1.4577	41.8	-	-
11	23.27	5.2	97.9	1.4567	36.6	122.1	1.4427
12	22.25	4.9	102.75	1.4558/9	31.7	-	-
13	22.52	5.0	104.95	1.4543/2	26.7	127.45	1.4398
14	22.17	4.9	112.25	1.4488	21.8	-	-
15	22.73	5.0	123.65	1.4400	16.7	132.15	1.4369
16	22.01	4.9	128.3	1.4378/7	11.8	135.8	-
17	19.81	4.4	131.75	14367/8	7.4	134.7	-
18	14.30	3.2	134.35	1.4367	4.3	135.55	1.4366/7
19	19.20	4.3	135.55	1.4366	0	-	-


1.4744 46 48 50 52 54 56 58 60 62 64 66
n_D^{60}
RUN No. 16.
(1) YIELD VS M. Pt. (2) YIELD VS n_D^{60}
FOR RESIDUAL WAX (WAX-OIL) IN SWEATER.
FIG. 41.
100%
75%
50%
25%
0%
PER CENT YIELD.
(2)
(1)
MELTING POINT (°F).
120 125 130 135 140

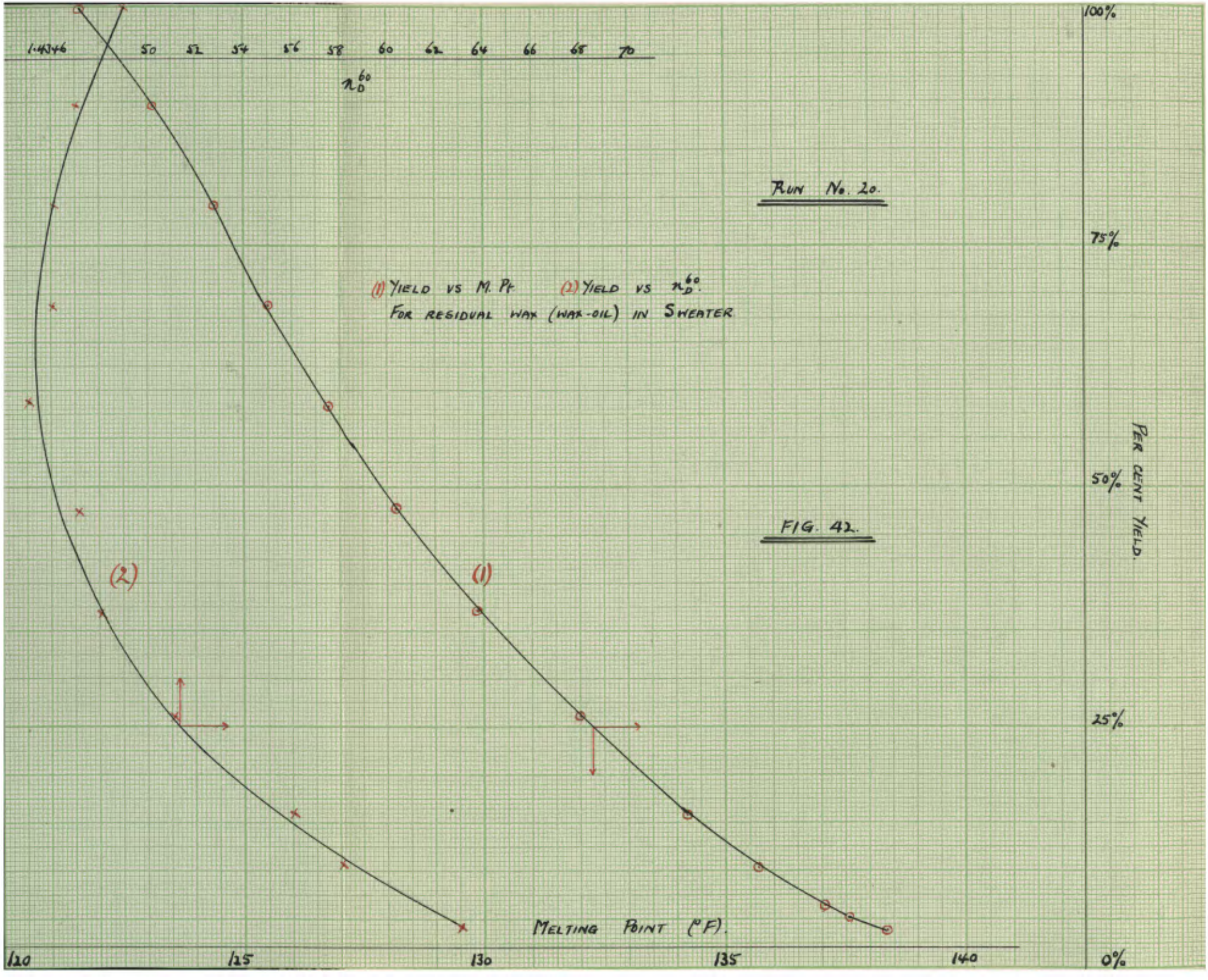
Experimental Run No. 16.

Properties of the Oil/Wax Mixtures.

Oil Content = 5%. M.P. = 120.4°F. n_d^{60} = 1.4366

Remarks. Normal process at 5% per

	LIQUID PHASE (SWEATED FRACTIONS)				RESIDUAL WAX (WAX-OIL) IN SWEATER		
Fraction No.	Wt.	%	M.P.	n_d^{60}	%	M.P.	n_d^{60}
0	-	-	-	-	100.0	120.4	1.4362
1	18.97	4.3	94.6	1.4500/1	95.7	-	1.4355
2	17.31	3.9	100.7	1.4448	91.7	122.3	1.4351
3	20.52	4.7	104.95	1.4411	87.1	-	-
4	21.31	4.8	108.35	1.4388/9	82.2	123.45	1.4347
5	24.17	5.5	112.1	1.4366/7	76.8	-	-
6	21.47	4.9	114.15	1.4353	71.9	124.8	1.4345
7	23.06	5.2	115.7	1.4349	66.7	-	-
8	22.46	5.1	116.75	1.4346	61.6	126.15	1.4344
9	20.89	4.7	118.0	1.4344	56.8	-	-
10	23.99	5.5	119.7	1.4342	51.4	127.5	1.4345
11	21.48	4.9	120.45	1.4342	46.5	-	-
12	23.08	5.2	-	1.4340	41.2	129.15	1.4346
13	20.28	4.6	122.5	1.4338	36.6	-	-
14	22.82	5.2	125.6	1.4339	31.5	131.0	1.4349
15	21.99	5.0	125.6	1.4342	26.5	-	-
16	24.56	5.6	127.5	1.4345	20.9		
17	23.34	5.3	129.45	1.4346/7	15.6	134.5	1.4355
18	21.77	4.9	131.05	1.4348	10.7	135.8	-
19	22.18	5.0	133.55	1.4354	5.6	137.9	-
20	16.06	3.7	136.55	1.4359	2.0	140.45	1.4364/5
21	8.65	2.0	140.45	1.4365			


1.4346
50
52
54
56
58
60
62
64
66
68
70
n_D^{60}
100%
75%
50%
25%
0%
PER CENT YIELD.
RUN No. 20.
(1) YIELD VS M. Pt. (2) YIELD VS n_D^{60}.
FOR RESIDUAL WAX (WAX-OIL) IN SWEATER
FIG. 42.
(2)
(1)
MELTING POINT (°F).
120
125
130
135
140

Experimental Run No. 20.

Properties of the Oil/Wax Mixture.

Oil Content = 2% M.P. = 121.55°F. n_d^{60} = 1.4350/1.

Remarks. Normal process at 5% per hour.

	LIQUID PHASE (SWEATED FRACTIONS)				RESIDUAL WAX (WAX-OIL) IN SWEATER		
Fraction No.	Wt.	%	M.P.	n_d^{60}	%	M.P.	n_d^{60}
0	-	-	-	-	100.0	121.55	1.4349
1	21.14	4.9	103.45	1.4411	95.1	-	-
2	22.55	5.2	108.8	1.4368	90.0	123.05	1.4347
3	22.48	5.2	111.8	1.4354	84.7	-	-
4	23.14	5.4	113.55	1.4346	79.3	124.35	1.4346
5	22.10	5.1	115.4	1.4340	74.2	-	-
6	22.88	5.3	115.95	1.4339	68.9	125.45	1.4345
7	22.51	5.2	117.1	1.4338	63.7	-	-
8	22.64	5.2	118.45	1.4337	58.4	126.7	1.4345
9	23.09	5.4	119.6	1.4337	53.1	-	-
10	22.74	5.3	120.85	1.4336	47.9	128.1	1.4347
11	23.02	5.3	120.2	1.4336	42.5	-	-
12	21.90	5.1	121.5	1.4338	37.4	129.85	1.4348
13	23.17	5.4	123.95	1.4341	32.1	-	-
14	25.88	6.0	125.65	1.4342	26.1	131.95	1.4351
15	23.21	5.4	127.5	1.4344	20.7	-	-
16	21.47	5.0	129.2	1.4347	15.7	134.15	1.4356
17	22.98	5.3	131.15	1.4350	10.4	135.6	1.4358
18	22.49	5.2	133.6	1.4354	5.2	-	-
19	5.44	1.3	135.15	1.4357	3.9	138.3	1.4363
20	16.96	3.9	138.3	1.4363	0	-	-

Experimental Runs 12-16 (incl) and 20.

Discussion of Results.

General Observation.

It was found that the presence of oil rendered the sweating much easier to control than in the experiments with oil-free wax. Little difficulty was experienced in reducing the temperature gradient in the wax-oil mass to 1°F, even in the stock containing only 2% oil.

This observation is of importance, as it is possible that any difficulties experienced with the laboratory sweater would be increased with industrial plant. It is possible that the presence of oil modifies the crystal structure of the wax in such a manner that sweating is facilitated. Other possible explanations may, however, be suggested.

The surface tension between solid and liquid wax may be less than that between solid wax and oil. Also, the viscosity of the oil is lower than that of the liquid wax and it is possible that the effect of these two properties is to allow the oil to flow more easily through the channels that are formed in the wax mass. Some evidence for the existence of these channels was found during the preparation of an oil-wax sample for one of the sweating experiments. The molten wax had been weighed into a beaker and had been cooled to a semi-

solid state such that when the oil was poured on to its surface, it did not immediately percolate through. After standing for one hour, however, the oil had passed through the mass, leaving the top surface with a honeycomb structure. This observation suggests that sweating may take place through capillary action and that these capillaries or channels are more easily formed when oil is present. The above is perhaps slightly outside the scope of these experiments but it is included as an item of interest, for it seems that no theory of the sweating process has so far been published.

Yield/Melting Point/Refractive Index Graphs. Figs. 37-42.

Owing to the large difference between the refractive indices of the dewaxed Second Cooled Blue Oil (n_d^{60}= 1.4867) and the various waxes obtained in the experiments (n_d^{60} = 1.4327 - 1.4372), the value of n_d^{60} for a wax-oil blend gives an indication of the oil content. The refractive indices of various blends of the dewaxed Second Cooled Blue Oil and the wax stock of melting point 122.1°F are given in Table XXIX below:-

TABLE XXIX.

% Wax	% Oil	n_d^{60}
100	0	1.4342
98	2	1.4350
94.9	5.1	1.4367
90	10	1.4386
80	20	1.4434
70	30	1.4486
60	40	1.4536
50	50	1.4589
30.1	69.9	1.4696
0	100	1.4867

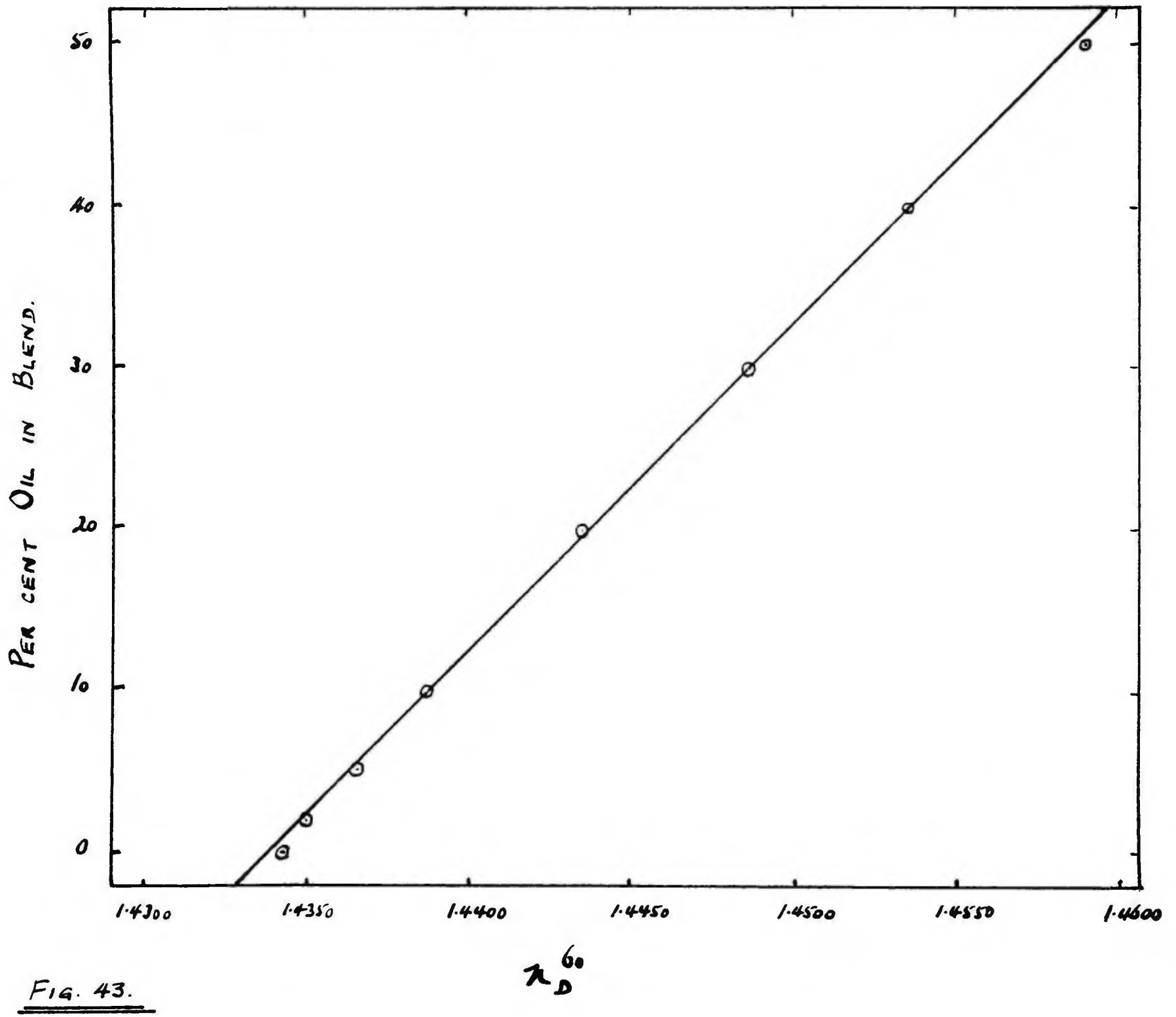

50
40
30
20
10
0
PER CENT OIL IN BLEND.
1·43·00
1·4350
1·4400
1·4450
1·4500
1·4550
1·4600
n_D^{60}

FIG. 43.

The graph of oil content/n_d^{60}, covering the range 0-50% oil, is shown in Fig. 43 opposite. The relation is linear over the range 10-40% oil, the equation to the straight line being

$$n_d^{60} = 1.4338 + 0.000492 \times \% \text{ oil.}$$

For oil contents higher than 50%, this relationship gives values of n_d^{60} that are too low. For example, according to this equation, n_d^{60} for the oil stock should be 1.4338 + 0.0492 = 1.4830, which is lower than the observed value of 1.4867.

Also, for oil contents of less than 5% the actual and calculated results differ, as there is a slight deviation from the straight line in this region. Unfortunately, it is in this region where a means of calculating the oil content would have been of special value in connection with this series of experiments. However, the values of n_d^{60} give other interesting information.

It is seen from Figs. 37-42 that the refractive index of the wax (wax-oil) remaining in the sweater decreases during the removal of the first fractions, reaches a minimum value, and then increases; the form of the curve being dependent on the amount of oil present in the original stock. The percentage of the wax (wax-oil) in the sweater at the stage corresponding with the minimum value of the refractive index is given for each run in Table XXX on the following page.

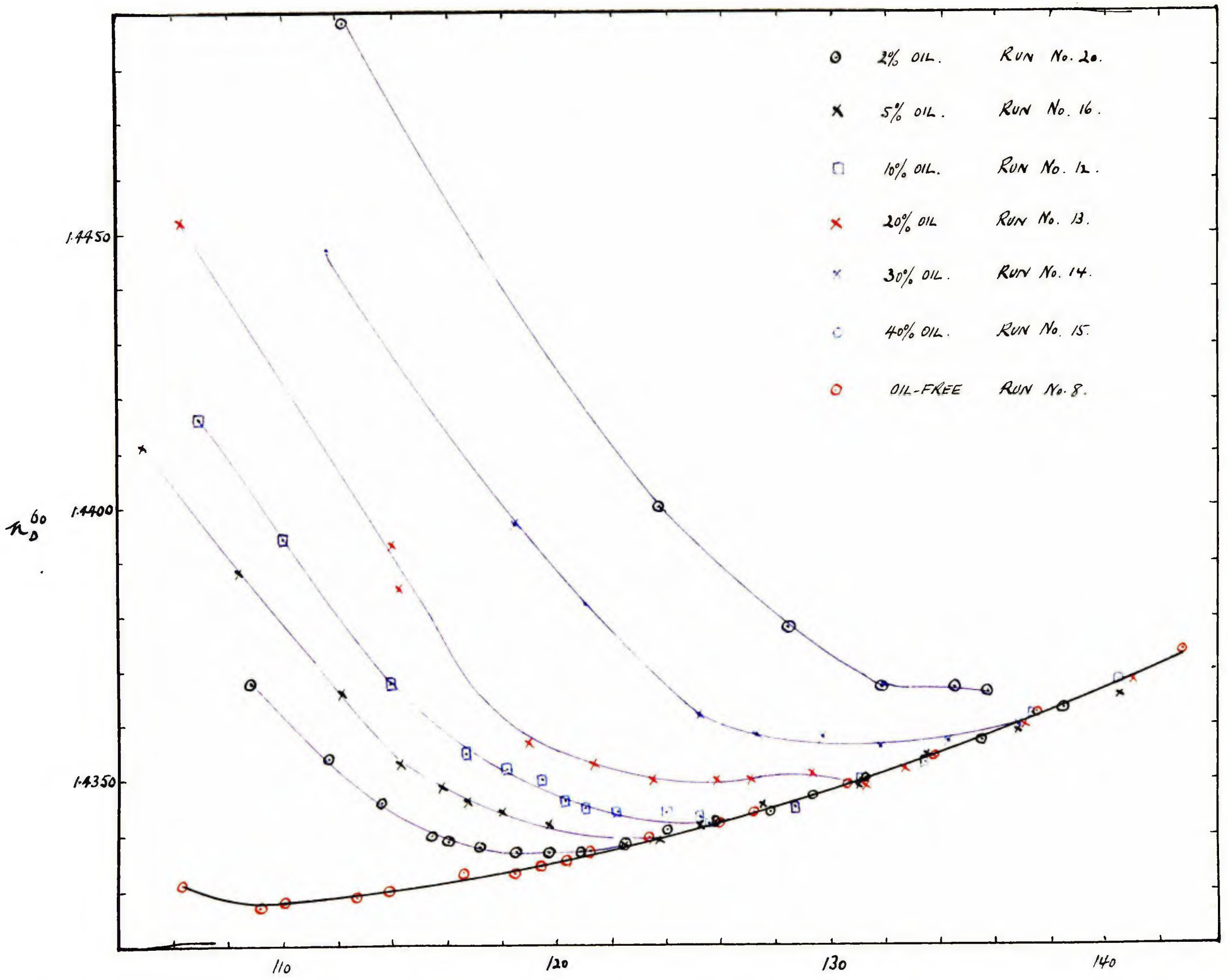

2% OIL. RUN No. 20.
5% OIL. RUN No. 16.
10% OIL. RUN No. 12.
20% OIL RUN No. 13.
30% OIL. RUN No. 14.
40% OIL. RUN No. 15.
OIL-FREE RUN No. 8.
n_D^{60}
1.4450
1.4400
1.4350
110
120
130
140
MELTING POINT. (°F).

FIG. 44.

Run No.	20	16	12	13	14	15
Oil Content of Stock.	2%	5%	I0%	20%	30%	40%
Minimum n_d^{60}	1.4346	1.4344	1.4347	1.4351	1.4358	1.4366
% of Stock in Sweater.	70	60/65	50	40	25	<5

The position of the minimum corresponds with the stage at which the removal of the oil is almost complete, and it is seen from Table XXX above, that the yields of oil-free wax (oil content probably less than 1%), independent of melting point, that may be obtained from the oil-wax mixture, depends on the original oil content of the latter.

The stage at which the oil has been almost completely removed from the stock is indicated in Fig. 44, in which the melting point is plotted against the refractive index at 60°C for each of the single liquid phase fractions of melting point higher than I00°F obtained in Runs 12-16 and 20. The corresponding graph for the fractions obtained in Run 8 (oil-free wax stock) is also shown. The curve for each run approaches this latter curve as the melting point of the fraction increases, until a stage is reached at which the two curves meet and then become almost co-incident. It is suggested that the two curves meet in each instance at the

stage where the oil content of the wax present in the sweater is somewhat less than 1%.

This figure of 1% is estimated as follows. It has been shown (Page 165) that the addition of 1% dewaxed Second Cooled Blue Oil to a wax of melting point 122.1°F increases the refractive index of the latter by approximately 0.0005. It is appreciated that the melting points of the waxes under consideration are higher than 122.1°F, but the error thus introduced is negligible in view of the small difference in the refractive indices of waxes of melting points 120°F and 140°F, compared with the refractive index of the oil. It may (be) therefore, assumed that the addition of 1% oil increases the refractive index of wax of melting point within this range by approximately 0.0005, an amount which would easily be detected with the Abbé Refractometer. It is seen from Fig. 44 that the curve for the fractions of corresponding melting points collected after the stage at which the curve for the run meets that for Run No. 8, does not deviate from the latter by more than 0.0002 in refractive index. It may therefore be concluded that the oil content of fractions in this region is considerably less than 1%. It is of interest to note from Fig. 44 that the curve for the wax stock originally containing 40% oil approaches,

but does not meet, the curve for Run No. 8. It is therefore to be inferred that, under the particular conditions of sweating employed in this investigation, it is not possible to obtain a substantially oil-free wax from stocks containing 40% or more oil.

With reference once again to the wax (or wax-oil) remaining in the sweater at a given stage, the refractive indices of waxes of various melting points higher than 125°F are given in Table XXXI on the following page for each of the runs. The corresponding values for the waxes obtained in Run No. 8 are also included for comparative purposes. The refractive indices of the various blended fractions obtained in this latter run were not found experimentally. However, the values have been calculated from those of the single fractions on the assumption that refractive index is additive over the limited melting range considered.

TABLE XXXI

MELTING POINT (°F).	REFRACTIVE INDEX AT 60°C. (n_d^{60})						
140	1.4367	-	1.4367	1.4366	1.4368	-	-
137.5	1.4362	1.4362	1.4361	1.4361	1.4361	-	-
135	1.4357	1.4357	1.4356	1.4357	1.4357	1.4361	1.4366*
132.5	1.4352	1.4352	1.4351	1.4352	1.4353	1.4358	1.4369*
130	1.4347	1.4348	1.4347	1.4348	1.4351	1.4358*	1.4383*
127.5	1.4345	1.4346	1.4346	1.4347	1.4353*	1.4368*	1.4398*
125	1.4342	1.4345*	1.4345*	1.4349*	1.4362*	1.4383*	1.4412*
Run No.	8	20	16	12	13	14	15
Oil Content of Stock.	0%	2%	5%	10%	20%	30%	40%

Those values marked with an asterisk fall on the "oil" side of the minima shown in the yield/refractive index graphs (Figs. 37-42).

Comparison of the values of n_d^{60} for the oil-wax experiments with the value of n_d^{60} obtained for the blended fractions of the same melting point in Run No. 8, shows that the Table may be divided into two sections:

(I) that in which the values of n_d^{60} for a given melting point are - within experimental error - the same, and

(2) that in which the values of n_d^{60} obtained in the oil-wax experiments for a wax of given melting point are higher than the corresponding values of n_d^{60} for the wax of the same melting point obtained in Run No. 8.

These two sections are indicated in the Table.

It is clear that the melting point of substantially oil-free wax (containing less than 1% oil) that may be obtained, depends on the oil content of the original stock; the higher the oil content, the lower is the melting point of the oil-free wax. It is of interest to note that even the highest melting point waxes obtained from the wax-oil stocks containing 30% and 40% oil respectively, contain oil to the extent of 1% or more.

Consideration of Yields.

The yield/melting point data given in Table XXXII below for the waxes included in Table XXXI are taken from Figs. 37-42, the yields being expressed as a percentage of the original stock (wax + oil). The yields of the corresponding waxes obtained in Run No. 8 are also included.

TABLE XXXII.

MELTING POINT (°F).	YIELD % (BY WEIGHT) Calculated as % of wax-oil stock.						
140	10.4	-	3.0	2.7	2.4	2.4	-
137.5	16.5	5.2	6.4	7.3	6.2	6.2	-
135	24.2	12.8	13.6	13.3	10.7	8.5	6.1
132.5	34.4	23.1	24.1	21.5	20.2	18.2	15.5
130	47.0	36.0	36.6	33.5	35.0	30.4	21.8
127.5	61.5	52.4	51.4	49.2	49.0	40.4	26.5
125	78.8	73.2	69.7	67.2	60.2	48.2	31.3
Run No.	8	20	16	12	13	14	15
Oil Content of stock.	0%	2%	5%	10%	20%	30%	40%

For comparison with the yields obtained in Run No. 8, the above yields should be calculated as a percentage of the total wax originally present in the wax-oil stock. The yields calculated on this basis are given in Table XXXIII below:-

TABLE XXXIII.

MELTING POINT (°F)	YIELD % (BY WEIGHT). Calculated as % of wax present in the wax-oil stock.						
140	10.4	-	3.2	3.0	3.0	3.3	-
137.5	16.5	5.3	6.7	8.1	7.7	8.9	-
135	24.2	13.0	14.3	14.8	13.4	12.1	10.1
132.5	34.4	23.5	25.3	23.9	25.2	26.0	25.8
130	47.0	36.7	38.4	37.2	43.7	43.4	36.3
127.5	61.5	53.4	53.9	54.7	61.2	57.7	44.2
125	78.8	74.7	73.2	74.6	75.2	68.9	52.2
Run No.	8	20	16	12	13	14	15
Oil Content of stock.	0%	2%	5%	10%	20%	30%	40%

The waxes containing less than 1% oil are shown above the dotted line, and general information concerning the yields of these products may be obtained from a consideration of the above figures (Table XXXIII) for oil-wax stocks of 2%, 5% and 10% oil content. In each of these

experiments the yields are very similar, although with the stock of 10% oil content they are slightly higher for waxes of melting point 135°F and above. It is difficult to explain this observation in view of the similarity of the yields of waxes of melting point 127.5° - 135°F. It is possibly due to experimental error caused by the inability to maintain uniform sweating at the desired rate with the comparatively small amount of solid present in the sweater at this stage.

Despite the relative ease with which sweating is controlled, the yields are considerably lower than those obtained in the fractional melting experiments with oil-free wax stock. In general, they are comparable with those given by the fractional melting of this oil-free stock at the rate of 15% per hour (See Table XXII Page 132), which was estimated to have an efficiency of 78% compared with the assumed 100% efficiency of Run No. 8. Fractional melting at the rate of 5% per hour was estimated on the same basis to be 90% efficient. Otherwise expressed, the yields of substantially oil-free (less than 1%) waxes of melting point 127.5°F and above, obtained from the wax-oil stock containing 2-10% oil, are in the region of 10-12% lower than those of corresponding melting point obtained by the fractional melting of the oil-free wax stock under the same conditions.

It is apparent that for products of melting point 127.5°F and above, the addition of 2% oil to the oil-free wax stock has the same effect as 10%. For products of lower melting point, there is a difference however, for their oil contents vary with the amount of oil initially present in the wax stock.

Generally, in view of the comparatively poor yields of lower melting point wax obtained from the oil-wax stock of 40% oil content, and also the failure to obtain a substantially oil-free wax of any melting point from this stock, it is suggested that an oil content of 40% is above the maximum for satisfactory sweating.

Assuming that one of the objects of sweating is to produce a substantially oil-free scale wax of melting point at least 127.5°F, there seems to be no advantage gained by reducing the oil content of the stock below 10%. Also, as the yield of this oil-free product from a stock containing 20% oil is relatively much lower than from one containing 10% oil, it is concluded that for satisfactory and efficient sweating, the oil content of the stock should be reduced to 10-15% by weight.

(2) Effect of Rate of Sweating. Experimental Run 21.

This run was conducted at the rate of 10% per hour. The wax-oil sample containing 10% oil was prepared in the normal manner, cooling taking place at room temperature overnight. The temperature gradient in the wax-oil mass during sweating could not be reduced below 2°F, otherwise the experiment proceeded normally.

Essential figures are given on the following page. The yield/melting point and yield/refractive index graphs for solid phase of melting point higher than 115°F are not given here, but they are very similar to those for Run No. 12, in which wax-oil stock, of the same oil content was sweated at the rate of 5% per hour.

The yields and refractive indices of waxes of melting point higher than 125°F remaining in the sweater at a given stage, are tabulated on the following page. For comparative purposes, the corresponding figures for Run No. 12 are also included.

TABLE XXXIV

MELTING POINT (°F)	Yield %	n_d^{60}	Yield	n_d^{60}
140	2.7	1.4366	3.0	1.4367
137.5	7.3	1.4361	6.6	1.4363
135	13.3	1.4357	12.9	1.4359
132.5	21.5	1.4352	22.2	1.4356
130	33.5	1.4348	33.5	1.4353
127.5	49.2	1.4347	48.8	1.4352 *
125	67.2	1.4349*	66.4	1.4356 *
Rate	5% per hour		10% per hour.	
Run No.	12		21.	

Those values marked with an asterisk fall on the "oil" side of the minimum found in each yield/refractive index graph.

Inspection of the above figures shows that, within experimental error, the yields are the same in each run, (cont. P. 178)

Experimental Run No. 21.

Properties of Oil-Wax Mixture.

Oil content = 10%. Melting Point = 118.7°F. n_d^{60} = 1.4386.

Remarks: Normal process at 10% per hour.

LIQUID PHASE (SWEATED FRACTIONS)					RESIDUAL WAX (WAX-OIL) IN SWEATER		
Fraction No.	Wt.	%	M.P.	n_d^{60}	%	M.P.	n_d^{60}
0	-	-	-	-	100.0	118.9	1.4388
1	21.53	5.0	87 *	1.4584	95.1	-	1.4375
2	22.54	5.2	96.5*	1.4516	89.9	121.05	1.4368
3	20.93	4.8	99.7	1.4471	85.0	-	-
4	23.81	5.5	105.45	1.4432	79.5	123.0	1.4361
5	25.74	5.9	109.35	1.4401	73.6	-	-
6	23.40	5.4	112.35	1.4382	68.2	124.75	1.4356
7	22.25	5.1	115.05	1.4371	63.1	-	-
8	22.91	5.3	116.25	1.4366	57.8	126.15	1.4353
9	22.60	5.2	117.7	1.4361	52.6	-	-
10	22.97	5.3	119.5	1.4357	47.3	127.75	1.4352
11	23.05	5.3	121.0	1.4351/2	42.0	-	-
12	22.31	5.1	122.25	1.4350	36.9	129.35	1.4353
13	22.93	5.3	123.65	1.4349	31.5	-	-
14	21.45	4.9	124.05	1.4348	26.6	131.5	1.4354/3
15	22.25	5.1	126.15	1.4348	21.5	-	-
16	22.22	5.1	128.4	1.4351	16.4	134.0	1.4357
17	22.01	5.2	130.3	1.4352	11.2	135.45	1.4360
18	22.00	5.1	132.6	1.4356	6.1	137.7	1.4364
19	14.52	3.3	135.7	1.4360	2.8	140.15	1.4367
20	12.02	2.8	140.15	1.4367	-	-	-

although the waxes of melting point below 135°F from the run at the faster rate are of slightly higher oil content than those of corresponding melting point from the slower run. Now there is no doubt that the yield of wax of a given melting point obtained from an oil-free wax stock is dependent on the rate of fractional melting. As a stage is reached in the sweating process where the wax mass is substantially oil-free, and the process thus becomes one of fractional melting, the similarity of the yields obtained in the two experiments under consideration is therefore rather unexpected. It is possible, however, that sweating at a rate considerably slower than 5% per hour would lead to increased yields of the various waxes.

(3) Effect of Method of Preparing Sample.

Experimental Runs 18 and 19.

Two runs were made for the purpose of investigating the extent to which the efficiency of the process is affected by the way in which the wax-oil sample is prepared prior to sweating. Wax-oil mixtures containing 10% oil were used in these experiments.

Run No. 18.

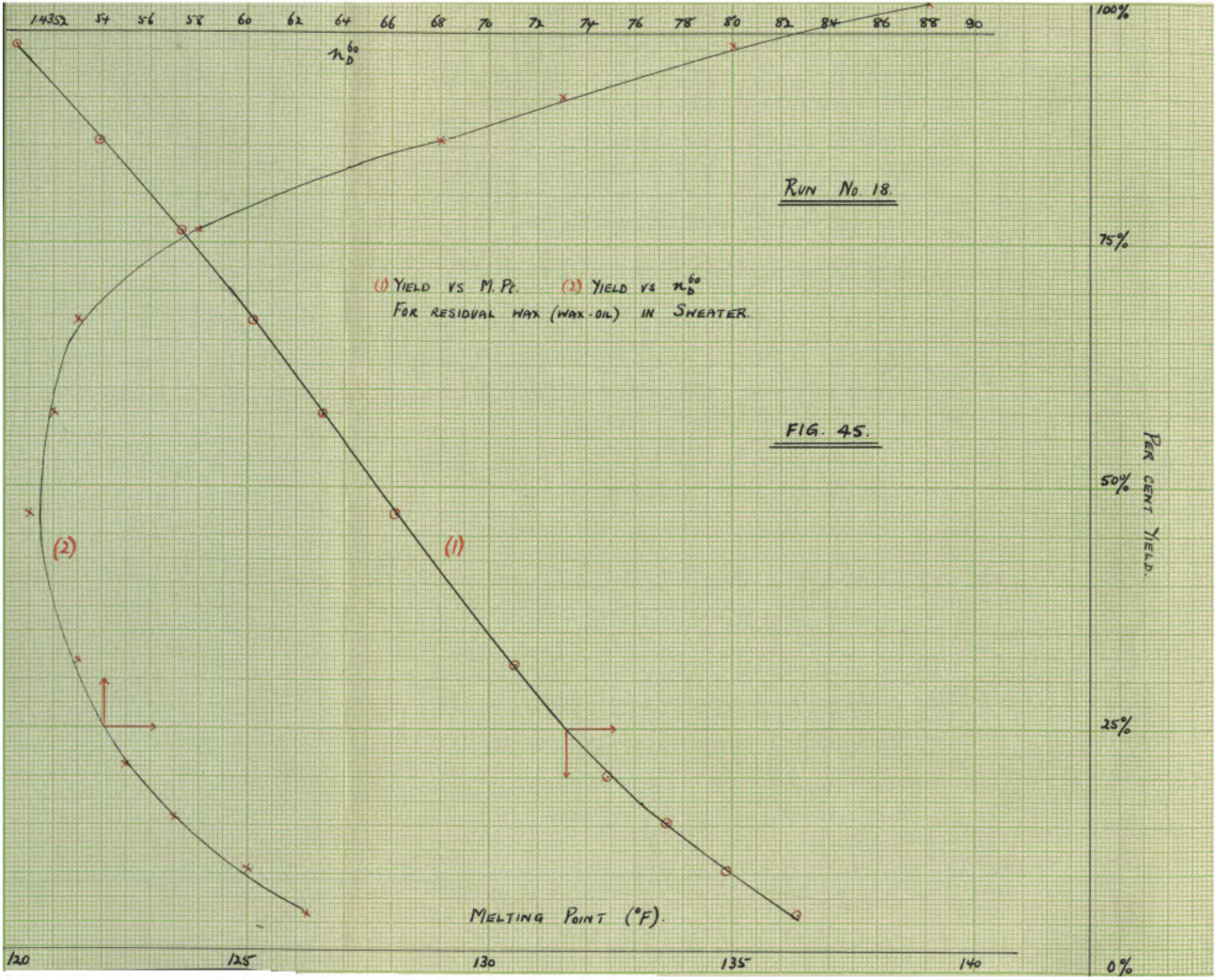
The sweater was prepared in the normal manner and the wax-oil sample introduced at a temperature of 130°F. Cooling took place in the absence of draughts until the central region of the mass was at a temperature of 87°F. At this stage, a temperature gradient of 4°F existed in the mass. The cellophane was then removed from the outer surface of the sweater and the latter placed inside the external heater, which had been heated so that the temperature of the air inside was 80-83°F. Sweating at the rate of 5% per hour was then conducted in the normal manner, the initial drops of liquid appearing in the collecting beaker after ten minutes' heating.

Run No. 19.

The sweater was prepared in the normal manner and the wax-oil sample introduced at a temperature of 135°F. The sweater and contents were immediately plunged into an acetone - solid CO_2 bath cooled to -50°C. The bath temperature quickly rose to -25°C and was maintained at -25°C — -30°C for one hour whilst the wax-oil sample solidified. On removal from the cooling mixture, the central region of the mass was at a temperature of 55°F. The sample remained at room temperature overnight, and sweating at the rate of 5% per hour was commenced on the following day.

The sweating appeared to proceed normally in each instance.

Essential figures for the two experiments are given in the two following pages. The yield/melting point and the yield/refractive index graphs (Figs. 45 and 46) for solid phase of melting point higher than 115°F are very similar for each run, and do not differ materially from those for Run No. 12, in which the wax-oil mixture containing 10% oil was sweated at the rate of 5% per hour after the usual procedure had been followed for the preparation of the sample.


1.4352
54
56
58
60
62
64
66
68
70
72
74
76
78
80
82
84
86
88
90
n_D^{60}
100%
75%
50%
25%
0%
PER CENT YIELD.
RUN NO. 18.
(1) YIELD VS M. Pt. (2) YIELD VS n_D^{60}
FOR RESIDUAL WAX (WAX-OIL) IN SWEATER.
FIG. 45.
(2)
(1)
MELTING POINT (°F).
120
125
130
135
140

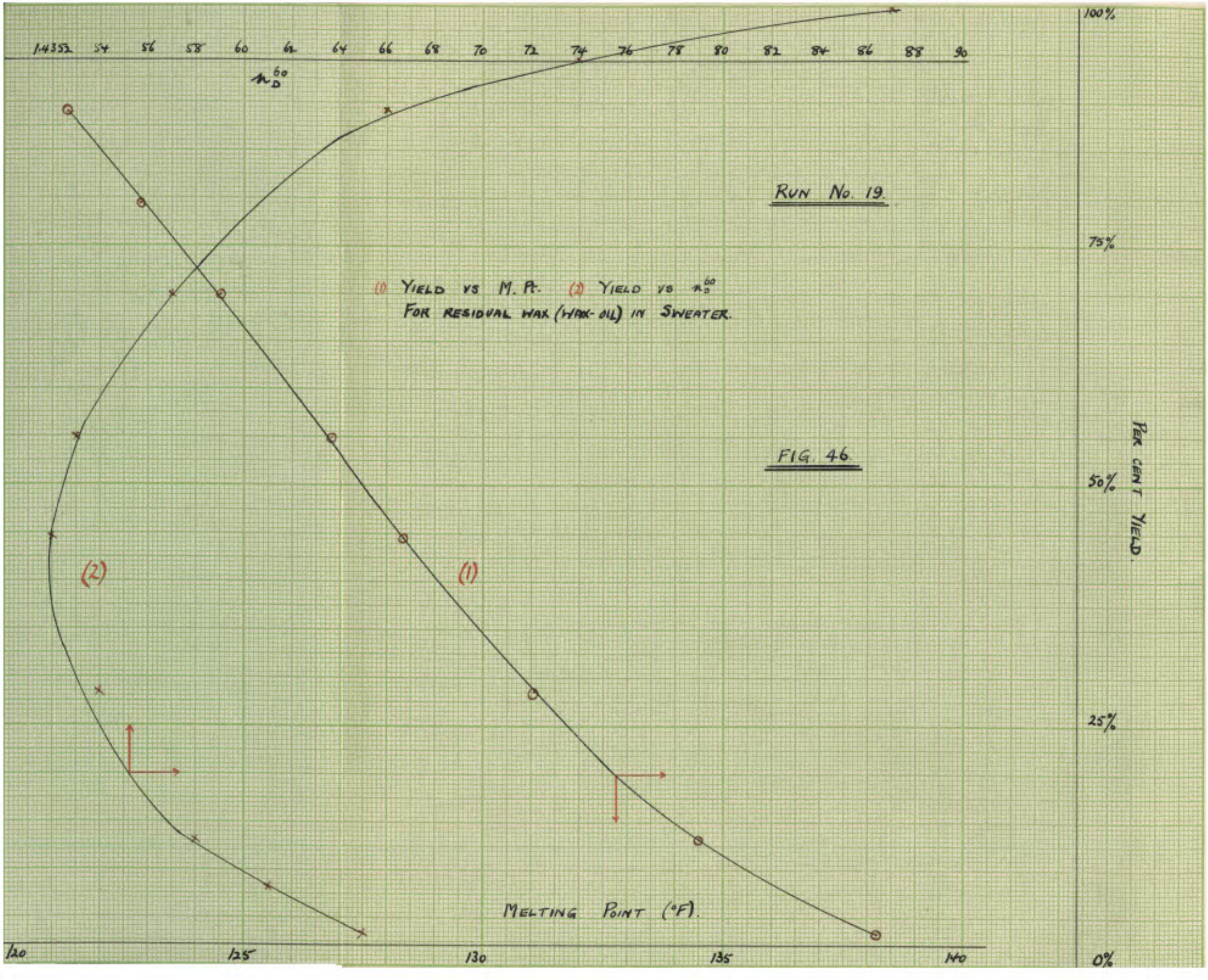
Experimental Run No. 18.

Properties of Oil-wax Mixture.

Oil content = 10%. M.P. = 118.7°F n_d^{60} = 1.4386.

Remarks. Normal process at the rate of 5% per hour after cooling sample to 82°F.

LIQUID PHASE (SWEATED FRACTIONS)					RESIDUAL WAX (WAX-OIL) IN SWEATER		
Fraction No.	Wt.	%	M.P.	n_d^{60}	%	M.P.	n_d^{60}
0	-	-	-	-	100.0	118.9	1.4388
1	19.41	4.5	88.5 *	1.4563	95.6	120.2	1.4380
2	22.99	5.3	94.5 *	1.4511	90.3	-	1.4373
3	19.53	4.5	96.5 *	1.4499	85.8	121.9	1.4368
4	19.44	4.5	101.4	1.4470	81.4	-	-
5	21.99	5.0	107.2	1.4420	76.3	123.65	1.4358
6	20.56	4.7	110.5	1.4393	71.6	-	-
7	19.64	4.5	113.75	1.4377	67.1	125.1	1.4353
8	21.14	4.8	116.2	1.4367/6	62.3	-	-
9	21.55	4.9	117.0	1.4362	57.3	126.5	1.4352
10	22.15	5.1	119.0	1.4356	52.2	-	-
11	22.58	5.2	118.05	1.4357	47.1	128.05	1.4351
12	21.85	5.0	121.4	1.4349/8	42.1	-	-
13	21.99	5.0	122.8	1.4346	37.0	-	-
14	23.30	5.3	124.25	1.4347	31.7	130.5	1.4353
15	22.29	5.1	125.55	1.4347/8	26.6	-	-
16	24.00	5.5	127.15	1.4350	21.1	132.45	1.4355
17	24.49	5.6	129.0	1.4351	15.5	133.65	-
18	21.75	5.0	131.05	1.4352	10.5	134.9	-
19	20.48	4.7	133.05	1.4356	5.8	136.35	1.4363
20	25.27	5.8	136.35	1.4363	0	-	-


1.4352 54 56 58 60 62 64 66 68 70 72 74 76 78 80 82 84 86 88 90
n_D^{60}
100%
75%
50%
25%
0%
PER CENT YIELD.
RUN No. 19.
(1) YIELD VS M. PT. (2) YIELD VS n_D^{60}
FOR RESIDUAL WAX (WAX-OIL) IN SWEATER.
FIG. 46.
(2)
(1)
MELTING POINT (°F).
120 125 130 135 140

Experimental Run No. 19.

Properties of Oil-Wax Mixture.

Oil Content = 10%. M.P. 118.7°F. n_d^{60} = 1.4386.

Remarks. Normal process at the rate of 5% per hour after "shock" cooling the sample at -25°C.

LIQUID PHASE (SWEATED FRACTIONS)					RESIDUAL WAX (WAX-OIL) IN SWEATER.		
Fraction No.	Wt.	%	M.P.	n_d^{60}	%	M.P.	n_d^{60}
0	-	-	-	-	100.0	118.9	1.4387
1	22.63	5.2	-	1.4669	94.8	-	1.4374
2	24.12	5.5	-	1.4511	89.4	121.3	1.4366
3	21.03	4.8	104.85	1.4432	84.6	-	-
4	21.19	4.8	107.85	1.4409	79.7	122.85	1.4360
5	20.09	4.6	110.3	1.4392	75.2	-	-
6	22.07	5.0	111.9	1.4381/0	70.1	124.5	1.4357
7	22.25	5.1	114.45	1.4369	65.1	-	-
8	22.21	5.1	116.2	1.4361	60.0	-	-
9	21.38	4.9	114.5	1.4368	55.1	126.8	1.4353
10	21.72	5.0	118.15	1.4354	50.2	-	-
11	22.85	5.2	120.05	1.4350	45.0	128.35	1.4352
12	26.04	5.9	121.6	1.4349	39.0	-	-
13	22.63	5.2	123.15	1.4347	33.9	-	-
14	22.01	5.0	124.5	1.4347	28.9	131.05	1.4354
15	21.90	5.0	126.05	1.4348/9	23.9	-	-
16	22.79	5.2	127.75	1.4350	18.7	-	-
17	22.74	5.2	129.45	1.4352	13.5	134.5	1.4357/8
18	21.79	5.0	131.4	1.4354	8.6	-	-
19	21.90	5.0	134.7	1.4359	3.6	138.2	1.4365
20	15.63	3.6	138.2	1.4365	0	-	-

Experimental Runs 18 and 19. Discussion of Results.

The yields and refractive indices of various waxes of melting point higher than 125°F remaining in the sweater at a given stage are given for Runs 18 and 19 in Table XXXV below. The corresponding figures for waxes obtained from the same stock at the same rate of sweating after preparation of the sample in the usual manner (Run No.12) are included for comparative purposes.

TABLE XXXV.

Melting Point (°F).	Normal Cooling.		Partial Cooling.		"Shock" Cooling.	
	Yield %	n_d^{60}	Yield %	n_d^{60}	Yield %	n_d^{60}
140	2.7	1.4366	-	-	-	-
137.5	7.3	1.4361	6.5	-	5.0	1.4364
135	13.3	1.4357	10.2	1.4360	12.0	1.4359
132.5	21.5	1.4352	20.4	1.4355	22.2	1.4355
130	33.5	1.4348	34.6	1.4352	34.9	1.4352
127.5	49.2	1.4347	50.5	1.4351	50.5	1.4353*
125	67.2	1.4349*	67.6	1.4353*	66.7	1.4356*
Run No.	12		18		19	
Rate.	5% per hour.		5% per hour.		5% per hour.	

Those values marked with an asterisk fall on the "oil" side of the minima found in the yield/refractive index graphs.

It may be observed from the Table(XXXV) that the yields of waxes of the same melting point obtained in the three runs are not very different. There is, however, an indication that the yields of waxes of melting point 135°F and above are slightly higher in the experiment involving normal cooling of the sample.

The slightly lower yields in the experiment involving partial cooling only of the sample might possibly be attributed to the wax crystals not having been allowed sufficient time in which to attain the size of those formed during normal cooling to room temperature (Run No. 12).

Rapid or "shock" cooling would almost certainly cause the formation of very small crystals, especially in the region of the wax-oil mass near the surface of the sweater, where the cooling conditions are most severe.

The refractive index data indicate that the residual waxes of melting point 125°F and higher, present in the sweater at any stage in these two runs, contain slightly more oil than those of the same melting point obtained in Run No. 12. It may be inferred from this observation that partial, as well as "shock" cooling, of the wax-oil sample causes the formation of small wax crystals, which are of such a nature that oil is less easily removed from them during the process of sweating.

The variations in the yields and refractive indices are not sufficiently great to allow any very detailed conclusions to be drawn.

It is clear, however, that the rate and extent of cooling of the sample prior to sweating have little effect on the efficiency of the process.

(4) Effect of Viscosity of the Oil - Experimental Runs 17, 22 and 23.

Oils of different viscosity for use with the oil-free wax stock in a study of the effect of viscosity on the sweating process, may be obtained as follows:-

(a) the viscosity may be varied by employing various oils of different boiling ranges, or

(b) the desired viscosity may be obtained by blending two dewaxed oils of high and low viscosities respectively.

The use of oils of different boiling ranges introduces complications due to the variation in chemical composition, and it was therefore decided to prepare oils of the desired viscosities from two stocks of dewaxed oils. This method ensures that the same constituents are present in each blend, although, of course, in different proportions.

Oil Stocks.

The dewaxed Second Cooled Blue Oil (see Page 150), used in the previous experiments, constituted the stock of low viscosity. The high viscosity stock was prepared from a "Master Lubricant" oil supplied from the A.I.O.C. Llandarcy Refinery.

The Second Cooled Blue Oil is normally obtained from the crude by cold pressing the light wax distillate, and the "Master Lubricant" is a heavier distillate taken from the crude immediately following the light distillate. This heavier distillate was dewaxed on the Refinery by treating with ethylene dichloride at -25°F using the Sharples process, but it was further dewaxed in the Laboratory by the method already described (Page 149) for the Blue Oil. The Laboratory dewaxing resulted in a very "sticky" or resinous oil having the following properties:-

Specific Gravity at 60°F = 1.010

Pour Point Below 0°C.

n_d^{60} = 1.5587

Viscosity: Redwood II at 100°F = 4,323 secs.

Redwood II at 140°F = 438.6 secs.

Blends covering a considerable viscosity range could therefore be prepared from these two stocks, and it was proposed to investigate the effect of oils over the complete viscosity range. However, the scheme was interrupted (September 1939) after completion of only two runs, the results of which are now discussed.

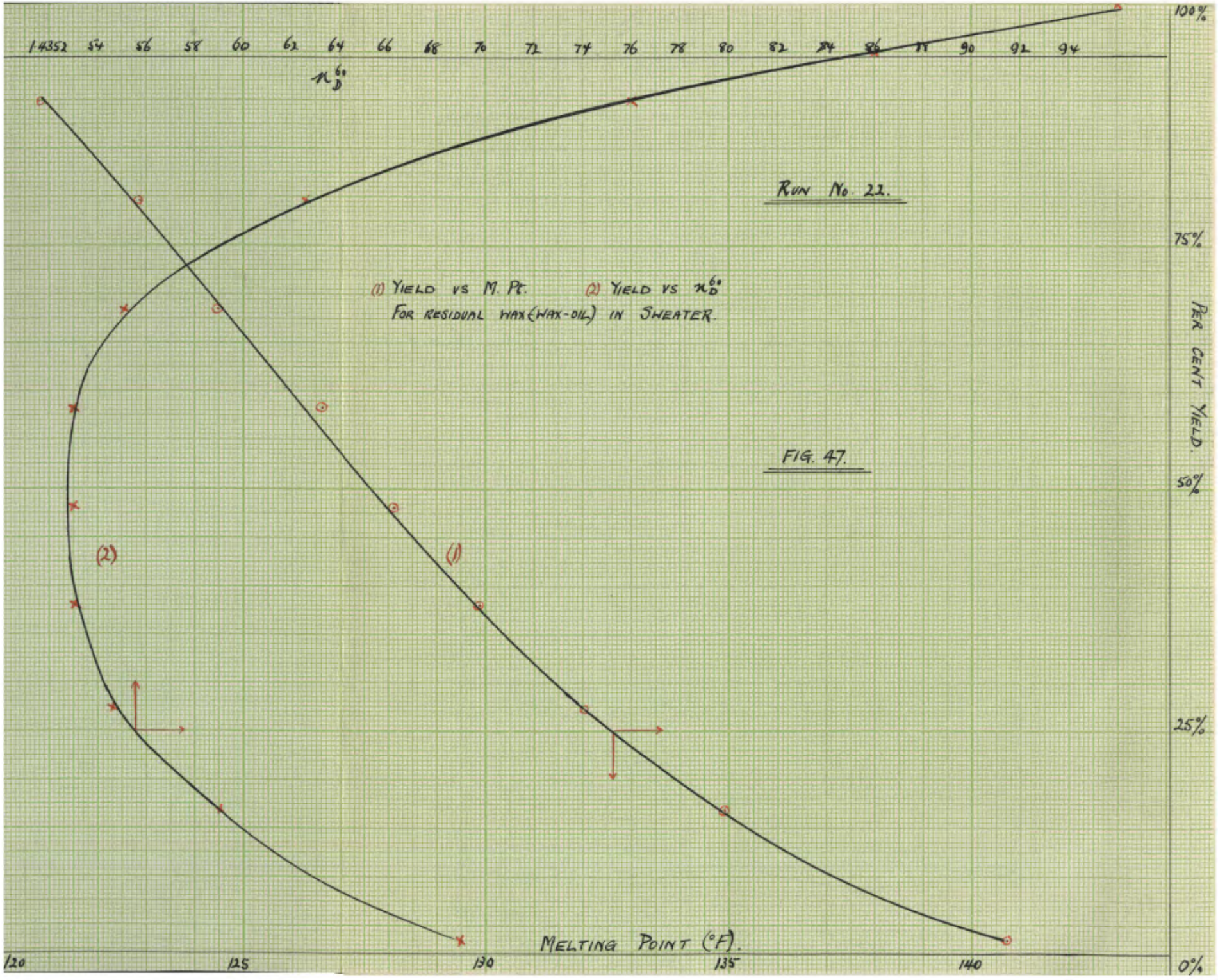
In view of the findings in the experiments with oil-wax stocks, it was decided to employ oil-wax stocks of 10%

oil content. In each instance, the sample was prepared in the normal manner, and sweating was conducted at the rate of 5% per hour. No difficulty was encountered with either stock.

Essential figures for each run are given in the following Tables, in which two additional abbreviations are used;-

D. B. O. = Dewaxed Blue Oil.

D. M. L. = Dewaxed Master Lubricant.


1.4352 54 56 58 60 62 64 66 68 70 72 74 76 78 80 82 84 86 88 90 92 94
n_D^{60}
100%
75%
50%
25%
0%
PER CENT YIELD.
RUN No. 22.
(1) YIELD VS M. PT. (2) YIELD VS n_D^{60}
FOR RESIDUAL WAX (WAX-OIL) IN SWEATER.
FIG. 47.
(1)
(2)
120 125 130 135 140
MELTING POINT (°F).

Experimental Run No. 22.

Properties of the Oil-Wax Mixture.

Oil Content = 10%. M.P. = 118.65°F. n_d^{60} = 1.4394.

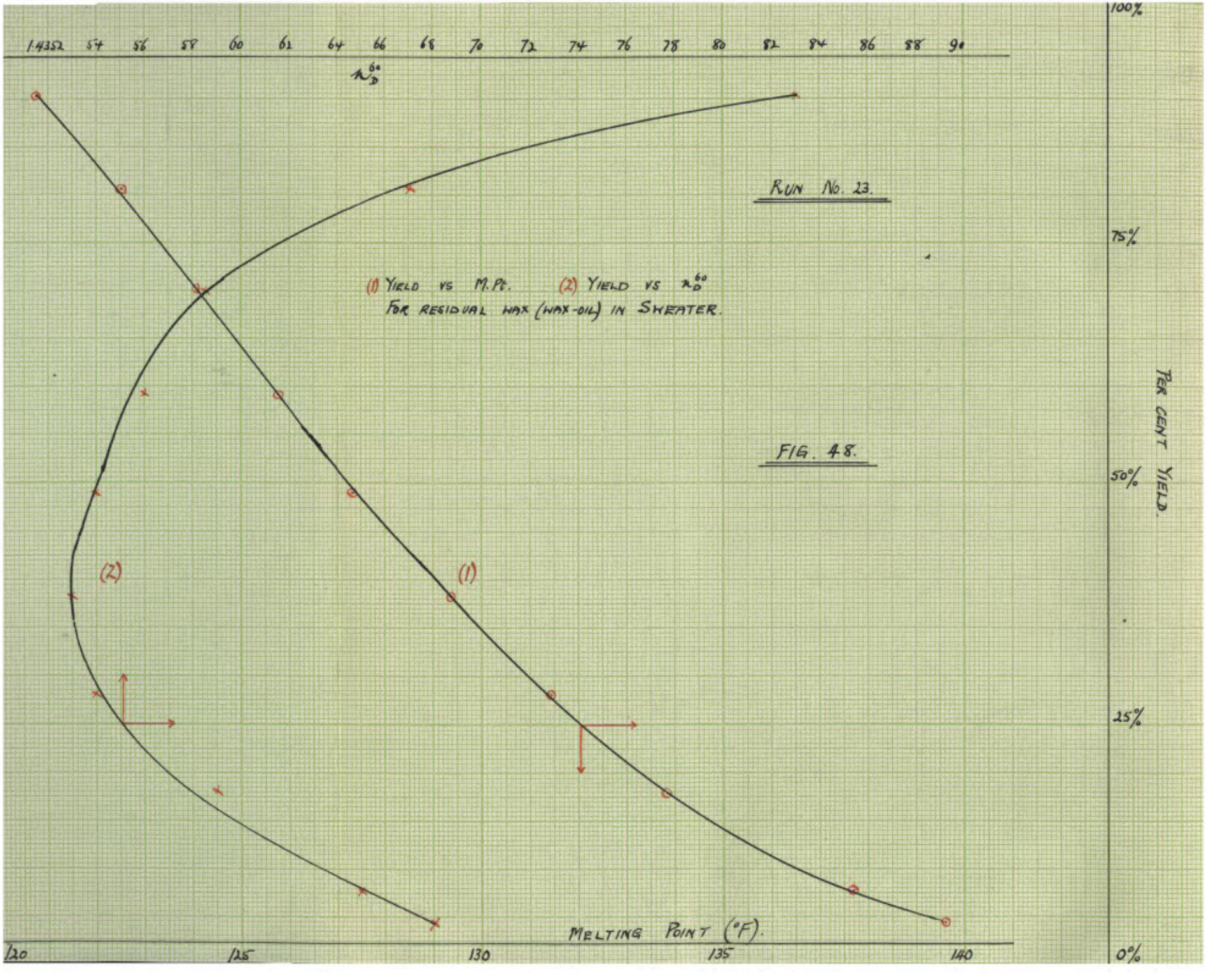
Properties of the Oil.

Composition: 90% D.B.O. + 10% D.M.L. Viscosity, Red. I at 70°F = 168.0 secs
Red. I at 100°F = 83½ secs

n_d^{60} = 1.4938.

Remarks. Normal process at 5% per hour.

LIQUID PHASE (SWEATED FRACTIONS)					RESIDUAL WAX (WAX-OIL) IN SWEATER		
Fraction No.	Wt.	%	M.P.	n_d^{60}	%	M.P.	n_d^{60}
0	-	-	-	-	100.00	-	1.4396
1	22.32	5.0	87 *	1.4609	95.0	-	1.4386
2	22.05	5.0	92.5*	1.4550	90.0	120.8	1.4376
3	22.46	5.0	97	1.4518	85.0	-	-
4	23.13	5.2	104.1	1.4457	79.8	122.85	1.4363
5	27.27	6.1	109.6	1.4405	73.7	-	-
6	22.70	5.1	113.0	1.4383	68.6	124.45	1.4355
7	23.32	5.2	114.85	1.4374	63.3	-	-
8	23.08	5.2	116.6	1.4366	59.1	126.6	1.4353
9	23.34	5.0	117.6	1.4359	53.1	-	-
10	22.44	5.0	118.9	1.4353	48.1	128.1	1.4352
11	22.65	5.1	120.3	1.4349	43.0	-	-
12	22.55	5.1	122.05	1.4348	37.9	129.85	1.4353
13	23.53	5.3	121.85	1.4345	32.7	-	-
14	23.17	5.2	125.3	1.4347	27.5	132.0	1.4354
15	23.00	5.2	126.35	1.4347	22.3	-	-
16	24.31	5.5	128.4	1.4351	16.8	134.9	1.4359
17	22.69	5.1	130.6	1.4354	11.7	-	-
18	23.48	5.3	133.6	1.4358	6.5	-	-
19	13.26	3.0	136.8	1.4362	3.5	140.7	1.4369
20	15.53	3.5	140.7	1.4369	0	-	-


1.4352 54 56 58 60 62 64 66 68 70 72 74 76 78 80 82 84 86 88 90
n_D^{60}
100%
75%
50%
25%
0%
PER CENT YIELD.
RUN No. 23.
(1) YIELD VS M.Pt. (2) YIELD VS n_D^{60}
FOR RESIDUAL WAX (WAX-OIL) IN SWEATER.
FIG. 48.
(2)
(1)
MELTING POINT (°F).
120 125 130 135 140

Experimental Run No. 23.

Properties of the Oil-Wax Mixture.

Oil Content = 10%. M.P. = 118.7°F. n_d^{60} = 1.4410

Properties of the Oil.

Composition: 70% D.B.O. + 30% D.M.D. Viscosity Red I. at 70°F = 445 secs.
Red I. at 100°F = 170 secs.

n_d^{60} = 1.5085

Remarks. Normal Process at 5% per hour.

LIQUID PHASE (SWEATED FRACTIONS)					RESIDUAL WAX (WAX-OIL) IN SWEATER		
Fraction No.	Wt.	%	M.P.	n_d^{60}	%	M.P.	n_d^{60}
0	-	-	-	-	100.0	118.8	1.4404
1	21.05	4.8	86 *	1.4683	95.3	-	1.4391
2	22.21	5.0	94 *	1.4607	90.2	120.75	1.4383
3	21.27	4.8	98 *	1.4544	85.4	-	-
4	22.22	5.0	105.5	1.4475	80.4	122.55	1.4367
5	23.15	5.2	108.55	1.4429	75.2	-	-
6	22.71	5.1	112.2	1.4405	70.0	124.1	1.4359
7	22.94	5.2	113.85	1.4392	64.8	-	-
8	25.04	5.7	115.7	1.4382	59.2	125.75	1.4356
9	22.29	5.1	117.0	1.4372	54.1	-	-
10	22.62	5.1	118.2	1.4364	49.0	127.3	1.4354
11	22.56	5.1	118.0	1.4362	43.9	-	-
12	22.95	5.7	121.3	1.4351	38.2	129.4	1.4353
13	22.88	5.2	123.25	1.4349	33.1	-	-
14	22.40	5.1	124.6	1.4349	28.0	131.45	1.4354
15	22.11	5.0	126.0	1.4350	23.0	-	-
16	22.52	5.1	127.6	1.4350	17.9	133.85	1.4359
17	22.44	5.1	-	1.4351	12.8	-	-
18	22.55	5.1	132.35	1.4355	7.7	137.7	1.4365
19	14.80	3.4	135.3	1.4361	4.4	139.6	1.4368
20	19.25	4.4	139.6	1.4368	-	-	-

Experimental Runs 22, 23 and 17. Discussion of Results.

The yields and refractive indices of various waxes of melting point higher than 125°F remaining in the sweater at a given stage are recorded in Table XXXVI. For purposes of comparison, the corresponding figures for Run No. 12 are included.

TABLE XXXVI.

Melting Point (°F)	10% D. Bo.		9% D. B. O. + 1% D. M. L.		7% D. B. O. + 3% D. M. L.	
	Yield %	n_d^{60}	Yield %	n_d^{60}	Yield %	n_d^{60}
140	2.7	1.4366	5.0	1.4368	(3.5)	(1.4369)
137.5	7.3	1.4361	10.0	1.4364	7.8	1.4365
135	13.3	1.4357	16.4	1.4359	13.8	1.4361
132.5	21.5	1.4352	25.5	1.4355	23.2	1.4356
130	33.5	1.4348	37.2	1.4353	34.6	1.4353
127.5	49.2	1.4347	52.2	1.4353*	47.8	1.4354*
125	67.2	1.4349*	67.0	1.4355*	63.7	1.4357*
Run No.	12		22		23	
Rate	5% per hour.		5% per hour.		5% per hour.	

Those values marked with an asterisk fall on the "oil" side of the minima found in the yield/refractive index graphs (Figs. 47 and 48).

The experimental data are insufficient for any general conclusions to be stated relating to the effect of the viscosity of the oil on the efficiency of the sweating process. However, the minimum values of n_d^{60} (Table XXXVI above) for Runs 22 and 23 are higher than for Run 12 and, moreover, correspond with a higher percentage of residual wax (wax-oil) in the sweater than for Run 12. These observations indicate that the oil of higher viscosity is more difficult to remove from the wax.

Experimental Run 17.

Before commencing the above experiments with oils of different viscosities, a run was made with a wax-oil mixture consisting of

70% oil-free wax, 15% D.B.O., and 15% Kerosene (Sp.Gr. at 60°F = 0.8025).

The sample was prepared in the usual manner and sweating was carried out without difficulty at the rate of 5% per hour. Essential figures for the run are given on the following page.

Experimental Run. No. 17.

Properties of the Oil-Wax Mixture.

Oil Content 30%. M. P. = 109.4°F. n_d^{60} = 1.4413.

Composition of the Oil.

50% D. B. O. + 50% Kerosene

(Sp. Gr. at 60°F = 0.8025)

Remarks. Normal process at 5% per hour.

LIQUID PHASE (SWEATED FRACTIONS)					RESIDUAL WAX (WAX-OIL) IN SWEATER.		
Fraction No.	Wt.	%	M. P.	n_d^{60}	%	M. P.	n_d^{60}
0	-	-	-	-	100.0	109.6	1.4415
1	21.08	4.9	-	1.4479	95.2	110.9	1.4413
2	21.38	4.9	85 *	1.4450	90.2	-	1.4411
3	23.09	5.3	91.5*	1.4446	84.9	112.7	1.4408
4	26.52	6.1	92 *	1.4442	78.8	-	-
5	22.13	5.1	- *	1.4439	73.7	114.65	1.4403/2
6	29.50	6.8	-	1.4432	66.8	-	-
7	23.28	5.4	-	1.4433	61.5	117.4	1.4396
8	21.61	5.0	-	1.4433	56.5	-	-
9	22.73	5.3	98*	1.4433	51.2	120.25	1.4387
10	22.74	5.3	98*	1.4435	46.0	-	-
11	21.16	4.9	99.5*	1.4431	41.1	124.3	1.4374
12	21.65	5.0	102.75	1.4427	36.1	-	-
13	20.39	4.7	107.8	1.4413	31.4	129.0	1.4360
14	21.73	5.0	118.9	1.4373	26.4	-	-
15	22.62	5.2	124.3	1.4359/8	21.1	-	-
16	21.26	4.9	127.65	1.4357/6	16.2	133.05	1.4359
17	23.51	5.4	130.8	1.4358	10.8	-	1.4360
18	22.70	5.2	133.1	1.4359	5.6	-	1.4361
19	17.04	3.9	134.85	1.4361	1.6	135.45	1.4362
20	7.01	1.6	135.45	1.4362	0	-	-

The comparison of the yields of various waxes obtained in this run with those obtained in Run No. 14, in which the oil-wax stock contained 30% D.B.O., is given in Table XXXVII below:-

TABLE XXXVII.

Melting Point (°F)	Yield % (By weight)	
140	2.4	-
137.5	6.2	-
135	8.5	4.8
132.5	18.2	18.6
130	30.4	28.2
127.5	40.4	35.2
125	48.2	39.8
Run No.	14	17
Oil Content of Stock.	30% D.B.O.	(15% D.B.O. (15% Kerosene.

The results of this run are included in order to mention the significance of the comparatively low yields of waxes of melting points 125° and 127.5°F obtained.

These low yields may be attributed to the higher solubility of the wax in the Blue Oil-Kerosene blend than in the Blue Oil alone. It is therefore suggested that any study of the effect of viscosity should be made in conjunction with experiments on the solubility relationships of the wax and the various oil blends employed.

Experiments on the Sweating of Oil-Wax Mixture - General Summary.

The principal findings from the Experimental Runs from No. 12 onwards concerning the effects of certain variables on the sweating process, may be summarised as follows:-

(I) The sweating of an oil-wax mixture is considerably easier to control than the fractional melting of an oil-free wax. This is of particular importance industrially, as ease of control of a process, especially on the commercial scale, is very desirable.

(2) The yields of the various melting point waxes, calculated as a percentage of the wax content of the oil-free wax stock, are considerably lower than for the corresponding waxes obtained by the fractional melting of this latter stock at the same rate.

(3) Under the same conditions of sweating, the efficiency of the process is dependent on the oil content of the stock. No advantage is to be gained by de-oiling the stock to an oil content of less than I0%. Also, the most satisfactory sweating stock contains I0-15% oil. At the other extreme, it is evident that an oil content of 40% is above the maximum for efficient and satisfactory sweating.

It will be appreciated, however, that these deductions are based on the results of experiments conducted at the same rate of sweating. It is possible, therefore, that a stock containing

40% oil could be satisfactorily processed at a considerably slower rate, especially during the collection of the first few fractions, when the loss of wax - due to solubility in the oil - would be reduced.

(4) The rate and extent of cooling of the sample prior to sweating has little effect on the yield and oil content of the various sweated, or scale, waxes produced.

(5) For corresponding melting points, the yields of waxes obtained by sweating at 5% and 10% per hour are similar, but those from the faster process are of slightly higher oil content. It is probable that a higher efficiency would result from sweating at a rate slower than 5% per hour, especially in the initial stages, when the oil content of the stock is comparatively high.

(6) The effect of viscosity has not been studied in detail, but in the limited experimental work performed on this factor, results have been obtained which indicate that oil of higher viscosity is more difficult to remove from the wax, and the resulting scale wax is therefore of higher oil content.

No experiments were made to ascertain the effect of over-heating in the wax-oil mass, as it is clear from the experiments with oil-free wax that strict control and regulation of the temperature throughout the mass is essential for satisfactory sweating.

C O N C L U S I O N.

It was stated in the introduction to this Thesis that the various stages of the work would be presented in the order in which they were completed. This plan has been followed, and the general conclusions from the experimental work have been given at the appropriate stages in Sections II and III. It is not proposed to make a re-statement of these conclusions, but a brief survey of the progress achieved is of interest.

The application of the idea of solid solution formation in the elucidation of the equilibrium diagram representing the fractional melting of wax mixtures, is an original contribution. Although the equilibrium diagram is of limited practical application, the explanation of its nature is of considerable academic interest, especially in connection with the general subject of solid solution formation.

The work on the relationship between melting point and molecular weight in the n-paraffin series, was developed (in conjunction with A. H. Etessam) as a result of difficulties involved in the application of Phase Rule principles to the study of solid-liquid wax, wax-oil, and wax-solvent equilibria. The "hypothetical" molecular weight of wax, derived from this relationship, has been applied with success in the main work,

but it is not claimed that it could be applied with equal success to any mixture of waxes. In view of the complex nature of wax, such a claim would be unjustified at the present stage of the work.

No reference may be found in the literature to experiments relating to the fractional melting of oil-free wax, and the results given in this Thesis represent a further original contribution. In this connection, it was intended to study the fractional melting of various mixtures of naphthalene and β-naphthol, two compounds which form a continuous series of solid solutions. The equilibrium diagram, which is of the type illustrated in Fig. 3 (Page 17), has been accurately determined, and an apparatus similar in design to, but considerably smaller than the sweater described herein, has been made. The work was interrupted before an actual experimental run could be made, and a more detailed account of this investigation has therefore not been included.

It was indicated in Section I that considerable work - with varying results - has been published on the many factors affecting the efficiency of the sweating of oil-wax mixtures. None of the previous workers on this problem has, however, employed synthetic mixtures of oil and wax, a method

of approach which overcomes difficulties associated with the variation in composition of the wax and oil constituents.

Finally - on the practical side - two useful pieces of apparatus have been designed, (I) a satisfactory and reliable sweater, and (2) an apparatus for separating the liquid and solid equilibrium phases formed by wax, or oil-wax, mixtures at any equilibrium temperature within their respective melting ranges.

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